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DUST PREVENTIVES

AND

ROAD BINDERS

BY

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PREFACE

THE object of this book is primarily to furnish road engineers with a working knowledge of the characteristic properties of dust preventives and road binders now in use, and to develop certain fundamental principles relative to their selection and application. During the past few years there has been a rapidly growing demand for such information, which has so far been met in a not altogether satisfactory manner. The subject of dust prevention and road preservation is at present in a transitional state, and there is unquestionably much yet to be learned regarding the effect of certain properties of road binders upon the results obtained in practice. It is hoped, however, that this work may serve as a basis for further development and that it will prove of some assistance to those who are interested in the use of such materials.

The conclusions as presented are based upon experience which the author has acquired both in the laboratory and in the field in the past five years of his service with the United States Office of Public Roads. During his connection with this office he has had under his personal supervision the examination of practically all varieties of road binders and their use under varying conditions in many parts of the United States.

Throughout this book the mention of trade names as applied to the results of examination of road binders has for the most part been purposely avoided for the reason that different lots of these products have not as a rule shown definite and uniform characteristics. The ideas of producers, with reference to the manufacture of their materials, are undergoing a process of evolution, and in spite of the present lack of uniformity it must be admitted that a general tendency is being exhibited toward the improvement of these materials.

vi PREFACE

The author here wishes to express his indebtedness to Mr. L. W. Page, Dr. A. S. Cushman and Mr. C. S. Reeve for their kind assistance and advice in the preparation of this book, and also to those authors, hereafter referred to, from whose works he has quoted.

Prévost Hubbard.

WASHINGTON, D. C., February 1, 1910.

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DUST PREVENTIVES AND ROAD BINDERS

CHAPTER I.

DUST PREVENTION AND ROAD PRESERVATION.

Introduction. — The prevention or suppression of road dust and the preservation of roads are undoubtedly two of the most important problems which to-day confront road engineers. Public attention in these matters has been aroused to such an extent that a demand for less dusty and more lasting roads than those of the past is becoming more insistent every day. In October, 1008, an International Road Congress met at Paris mainly for the purpose of considering these two problems. From the mass of data contained in the proceedings of this Congress one important fact stands prominently forth, that the solution of these problems lies in the treatment of both old and new roads with chemical For confirmation of this fact one has only to substances. consider the rapid growth of the chemical road preparation industries both in numbers and in importance during the past four years.

While the purpose of this book is to treat of chemical road materials, a proper understanding of the value and practical use of such substances cannot be attained without a thorough knowledge of the causes and effects of road dust formation and road deterioration, and the relations existing between them.

This chapter will, therefore, deal with the various phases of these two most important road problems and in later chapters their close relation to the subject of dust preventives and road binders will be developed.

The Dust Problem. — It has been said that nine-tenths of the dust produced by man originates on his roads and streets. While this is a difficult matter to estimate with any degree of accuracy, it is nevertheless true that a large proportion of dust produced by man undoubtedly comes from this source, and equally true that far more havoc is wrought by road dust than is generally realized. The formation of road dust in excessive quantity has given rise to what has been termed in recent years the dust nuisance, and many articles have appeared in the press from time to time calling attention to this matter. The subject has, to a great extent, been discussed from individual standpoints and presented to the reading public in fragmentary form, and while these articles have undoubtedly awakened some interest, the attitude taken in regard to its importance is far from being what it should. It is not only as a public nuisance that dust should be considered, but as a public menace which is striking directly at the life of many individuals and in various insidious ways is lessening public comfort and public health. Much money, both public and private, has been spent in attempts to remedy the damages caused by dust, a part of which might better have been used in curing the cause rather than the result.

Since the memorable work of Pasteur upon the origin of certain microscopic organisms, thousands of scientists have studied the characteristics and habits of these active mites of the invisible world which surrounds us. As early as 1876, Tyndall, in a discourse upon Fermentation delivered before the Glasgow Science Lectures Association, showed the distribution of these organisms to be closely associated with the transportation of dust, and subsequent study has proved only more conclusively the truth of his assertions. It is now a well-recognized fact that in dustless air these organisms do not exist, while under otherwise similar conditions they are found in increasing numbers as the amount of dust in the air is increased. When previously sterilized, milk will not sour in dustless air no matter how warm it may be, meat will not putrefy, and likewise germ diseases cannot be contracted from this source. In dusty air, however, the

bacteria of milk fermentation and of meat putrefaction will, under favorable conditions, quickly spoil the milk and meat, while the presence of countless other germs increases to a great extent the probabilities in mankind of contracting various forms of disease. These germs readily attach themselves to dust particles and the slightest current of air then distributes them throughout the atmosphere where their war upon mankind is waged. Among the many diseases contracted from breathing dust laden air mention of but one, tuberculosis, should be sufficient to interest every intelligent reader in the problem of dust suppression. When the true effect of dust upon public health is fully realized, the statement of Tyndall "that all the havoc of war, ten times multiplied, would be evanescent if compared with the ravages due to atmospheric dust," can well be believed.

The effect of road dust upon some classes of live stock is also most severe, cattle and horses in particular being susceptible to the germs of tuberculosis which it carries. In certain districts devoted to the raising of horses it has been noticed by breeders that since the advent of the fast moving motor car, with its great dust raising propensities, this disease has been much more prevalent among their stock than in the days when excessive road dust formation and its aërial transportation was of less common occurrence.

The personal discomforts to which those using and living near dusty roads are subjected are too well known to need discussion. Clothing and household furnishings are damaged, while yards and verandas are aften made untenantable. For these reasons alone real estate in certain localities has depreciated in value to a considerable extent within the last few years, it being a difficult matter to find tenants willing to put up with the annoyances and inconveniences resulting from the road dust.

Its effect in large quantities upon vegetation is disastrous in the extreme and in many fruit growing districts such loss has resulted from this source that no attempt is now made to raise fruit near dusty roads. The distribution of road dust over plants and shrubbery, besides making them unsightly, clogs the breathing pores of the leaves, retards their growth, and in some instances has been known to kill large trees.

While some classes of roads and pavements are benefited by the removal of dust, others are greatly damaged by this means. The macadam is a good example of the latter class, one of the fundamental principles of this form of construction being that the life of the road is dependent upon the retention of the fine products of wear which serve to bind together and hold in place the coarser fragments of stone constituting the wearing surface. Both of these facts at once connect the dust problem with that of road preservation. Before taking up these relations in detail, however, it may be well to briefly consider the more important causes of dust formation on roads.

Causes of Dust Formation on Roads.—Broadly speaking, dust is matter in a finely divided state produced by the application of energy upon matter in a compact state. The result of this energy is usually termed wear. Dust may therefore be considered as the product of wear, and wear as the fundamental cause of dust formation. Other factors which tend to remove and distribute dust when formed, thus exposing fresh surfaces to wear, should, however, be considered in this connection. All forces which tend to disintegrate or destroy roads will of necessity produce wear and these forces may be conveniently divided under three heads, chemical, physical and mechanical.

In regard to chemical agencies, it has long been known that water carrying small amounts of carbonic, humus, and other acids is capable of slowly decomposing many minerals found in the rocks commonly used for road building, and, as it is mainly the treatment of stone roads which will be considered in this book, a brief review of the character of the reactions involved may not be out of place at this point. Besides these weak acids it has been found that water alone is capable of acting chemically upon many rock constituents, causing the breaking down into secondary products of the primary minerals, especially. While it is true that this action is at first very slight, it proceeds at a more rapid rate as the road material becomes

finer, and, as it is almost constant, in the end produces considerable effect. Thus the feldspars, which are of very common occurrence in road materials, are partly broken down into kaolin or other secondary products with the solution and partial removal of the soluble material also formed. While this action tends to disintegrate the rock, it, like many of the other causes of wear, often exerts a somewhat beneficial effect upon the road, the secondary products in certain cases being of a colloid or gluelike character, and therefore capable of binding the fragments of undecomposed material together. A detailed study of these reactions will be found in publications of the Department of Agriculture, by Page, Cushman and Hubbard on * " The Cementing Power of Road Materials" † "The Effect of Water on Rock Powders" and t "The Decomposition of the Feldspars." Another way in which the chemical action of water sometimes acts to advantage in consolidating a road surface is in the formation, through solution and evaporation, of crystal bodies such as calcite which, upon crystallization, forms a more or less rigid bond. In some instances, a combination of these reactions takes place with the formation of both colloid and crystalloid bodies which interlock and produce a sort of set similar to that which takes place in Portland cement. The action of water upon certain slags presents a good example of this kind of reaction.

The most important physical agencies which tend to hasten wear and therefore the formation of dust are (1) the disrupting effect of frost, (2) the attrition of falling rain, (3) the transporting power of water, and (4) the action of wind. The effects of frost and wind are of course much more important than the effects of rain and running water, and have to be considered in particular when treating a road with reference to dust prevention. It may be added that in selecting a material which shall act as a permanent dust preventive, care should be taken to

^{*} U. S. Dept. of Agric. Bureau of Chemistry Bull. 85.

[†] U. S. Dept. of Agric. Bureau of Chemistry Bull. 92. ‡ U. S. Dept. of Agric. Office of Public Roads Bull. 28.

obtain one which will make the surface as nearly waterproof as possible, especially in localities where the winters are long and severe.

The action of wind has an important bearing upon the prevention of dust, although it has a somewhat indirect relation to dust formation. If all of the products of wear were retained on the road surface, or if these products were removed in a manner similar to that caused by running water, we should experience but little difficulty with our roads. The removal of fine material without doubt hastens wear by exposing surfaces which would otherwise be protected by a cushion of the products already formed, but, if these products were not susceptible to the action of wind, there would be no dust problem. The action of wind, therefore, can be considered as one of the most direct causes of the dust nuisance.

The mechanical agencies are abrasion, impact, local compression and shear. All of these forces are in a great measure due to traffic; abrasion to the grind of steel-tired wheels, impact to the action of horses' hoofs, local compression to heavily loaded narrow tired wheels, and shear to the tractive force exerted upon the road surface by the wheels connected with the driving mechanism of self-propelled vehicles. In respect to the first two, abrasion and impact, considerable judgment can be exercised by the road builder as to the selection of materials which will best withstand these forms of attack. For this purpose certain physical tests, with which most road engineers are familiar, are employed in order to determine the comparative value of different rocks with respect to their hardness, toughness, and resistance to wear. Descriptions of these tests will be found in most textbooks dealing with the construction of macadam roads and need not here be considered in detail. By making use of such tests the road engineer can, to a great extent, foretell the wearing properties and other characteristics of any road stone which he wishes to employ, and, as will be shown later, a knowledge of these properties will prove of considerable value in enabling him to select a proper dust

preventive or binder for use with the particular kind of rock of which the road has been or is to be constructed.

One other cause or source of dust on roads is the transportation or deposition of extraneous material which may previously exist as dust or which, under the action of the forces described above, is converted into dust upon the road surface. This is a phase of the problem commonly encountered in thickly settled districts and often requires quite different treatment from the others which have been mentioned. This point will be treated in detail in a later chapter.

Relation of the Dust Problem to That of Road Preservation.—Upon reviewing the causes of dust formation it is clearly apparent that most of them have a direct bearing upon road deterioration, and that the problem of dust prevention is, therefore, closely associated with that of road preservation. While this has come to be a well-recognized fact, it may not be amiss to consider their relation as applied to different types of roads. For this comparison roads may be classified under the following three headings: (1) earth roads; (2) broken stone and gravel roads; (3) pavements.

Earth roads being composed entirely of finely divided material, it is evident that most of the forces which produce dust, and therefore wear, will exert a greater destructive effect upon them than upon the other types of roads. Because of this property they are also apt to have but little inherent mechanical stability, and this fact should never be lost sight of when attempting to prevent deterioration by the application of a dust preventive or road binder. Owing to their high absorptive capacity, water or any other liquid in large quantities lowers their mechanical stability, although in moderate quantities these agents may act as binders. Frost and the transporting power of water are the most important physical agencies which tend to cause deterioration in earth roads, and local compression and shear the most important mechanical forces.

Broken stone and gravel roads have considerably greater mechanical stability than earth roads, and when properly constructed, therefore, suffer less from all but one of the causes of deterioration of the latter. Macadam roads in particular are designed to withstand the rapid destructive effects of water, abrasion, impact, and local compression and in fact make use of these forces to a great extent in self-repair. They are not, however, capable of successfully resisting the shearing stresses to which they are subjected by motor traffic, and this fact is the fundamental cause which has aroused such a widespread interest in the problems of dust prevention and road preservation, and which bids fair to revolutionize the ordinary form of macadam construction.

Pavements have the greatest mechanical stability of any of the three types of roads mentioned, owing to the presence of a more or less rigid binding material, or to regularity in the setting of their integral parts. They are the most resistant to all of the forces which produce dust and deterioration and are for the most part fairly satisfactory in this respect, although they slowly succumb to these forces unless repaired. The formation and deposition of dust upon their surfaces from outside sources, however, often accelerates deterioration, especially in the case of bituminous pavements, and so this last cause of dust formation is shown to be closely associated with the problem of road preservation, as are all of the others. The evolution of the city pavement from the earth road has been a partial solution of both the problems of road preservation and dust prevention, and teaches a lesson that should prove of great value in the further consideration of the contents of this book.

Effect of Automobile Traffic on Roads.—It has come to be a well-recognized fact that the automobile is the most potent factor which at the present time operates to produce dust and destroy roads. During the past two years much study has been devoted to determining the actual cause or causes of the damage produced by this class of traffic, and a number of interesting theories have been advanced concerning them. Perhaps the most noticeable effect produced by the passage of an automobile over the surface of a road is its dust raising propensity. Another

fact that is apparent to the most casual observer is that upon a given road this property is proportional to the speed at which the machine is driven. When moving at a moderate rate but little dust is raised, in fact no more than would be produced by other classes of traffic. As the speed is increased to fifteen miles per hour and over, however, the dust cloud following in the wake of the vehicle is seen to grow larger and larger. The same effect may be observed from the passage of a railroad train over steel rails if the route lies through a dusty country. This is caused by the formation of a partial vacuum and consequent air currents behind the rapidly moving body, which whirl aloft any fine material with which they come in contact and eventually scatter it over the surrounding country.



Fig. 1. Macadam Surface Stripped of Fine Material by Automobile.

It has been claimed that a similar vacuum effect is produced by the rapid passage of pneumatic tires over a road surface, but this would appear to be but slight in comparison to that produced behind the body of the car itself. An examination of almost any old macadam road which has been subjected to heavy automobile traffic will show that much more damage has been wrought than can be accounted for by the removal of surface dust alone. Large fragments of rock constituting the wearing surface and even the lower course are found to be displaced and in some instances thrown up in windrows running longitudinally with the road. In extreme cases the whole surface has become disintegrated and only a loose mass of broken stone marks the former site of the once well-bonded road. This effect is well illustrated by Fig. 1, which shows a macadam road that has been practically destroyed by automobile traffic.

It would seem, therefore, that some forces other than induced air currents are responsible for this damage. Two notable reports dealing particularly with this phase of the subject were presented at the First International Road Congress in 1908, one by L. W. Page,* Director of the United States Office of Public Roads, and the other by M. A. Petot,† Professor of the Faculty of Sciences of Lille. The conclusions presented in both of these papers were quite similar and undoubtedly explain the chief cause of the destructive action of motor traffic on road surfaces.

To quote from the former — "As already stated, the broken stone road has been developed to withstand the wear of irontired horse vehicles, and has met successfully the demands of suburban and rural traffic until the advent of the motor vehicle. When in its highest state of perfection, the rock from which such a road is made is so suited to the volume and character of traffic which passes over it, that the amount of dust worn off is only sufficient to replace that removed by wind and rains. . . . When such a road is subjected to continuous fast motor traffic, entirely new conditions are brought about. . . . Beyond a doubt this most injurious action of motor traffic is the great tractive or shearing force exerted by the driving wheels of these cars. The fine dust which ordinarily acts as a cementing agent to the road surface is thrown into the air to be carried off by the wind, or

^{*&}quot;The Effect of Modern Traffic on Broken Stone Roads."

^{† &}quot;Effets des Nouveaux Modes de Locomotion sur les Chaussées."

that remaining on the road is so loosened that it is easily washed into the gutters by rain. The pneumatic rubber tire wears off from the broken stone of the road little or no dust to replace that thus removed, and the result is that the stones become loose and rounded, giving the greatest resistance to traction and allowing water to make its way freely to the foundation of the road. . . . To sum this matter up briefly, the pneumatic tire, or any type of tire which propels a vehicle, must have sufficient tractive resistance to overcome the load of the vehicle. This, of necessity, must cause a shear on the road surface which varies with the weight and speed of the vehicle. The broken stone road surface has little power to resist a shearing stress, consequently the fine material of which it is composed is thrown into the air. . . . Aside from the dust carried from the road in this manner, this shearing force of the motor car has a decided disintegrating effect on the surface of the road."



Fig. 2. Action of Fast Moving Motor Car upon Road Surface.
(Speed 80 miles per hour)

The destructive action exerted by the rear wheels of a motor car moving at high speed is very plainly shown in Fig. 2.

While the vacuum effect and direct shearing force produced by rapidly moving automobiles are the most important causes of dust formation and road deterioration, mention should be made of the side slip and skidding effect of the tires, especially upon curves. This action, while somewhat reduced by anti-skidding devices, is often terribly destructive when it does take place, particularly in cases where armored tires are used. When pronounced irregularities occur in the surface of roads the automobile is also apt to cause considerable damage, for a small hole once started grows rapidly under its action, especially in wet weather, owing to the sloughing effect of the heavily tired wheels which throw the accumulation of water and mud out of these holes upon the road surface.

The amount of damage which the automobile has already done to macadam roads can best be demonstrated by a glance at official reports on this subject, obtained from various sources. Thus, in England, seven counties near London report that the percentage of increase of cost of care and maintenance, claimed to be due to the use of the automobile, has been from twenty-two to seventy-seven per cent. Statistics of the Massachusetts Highway Commission show that about fifty-three per cent of the destruction of state highways is due to automobiles, and reports of a similar nature have been made by French engineers.

Earth roads, having less mechanical stability than any other type of road, are, of course, greatly damaged by the automobile, and dust formation is invariably excessive on such roads which are subjected to even a moderate amount of motor car traffic.

It is only upon street pavements that motor vehicles produce no observable deterioration. In fact this class of traffic here seems to be less injurious than any other, owing to the great resistance offered to shearing stresses by the pavement itself, and to the protective action of the rubber tires which reduces impact and abrasion to a minimum. Because of the continued deposition of extraneous material upon the surface of the pavement, however, much dust is often produced by these vehicles, so that even here the problem of dust prevention exists. The automobile is, therefore, invariably held responsible for the dust nuisance if not for road deterioration.

While, as has been shown, the automobile is undoubtedly to blame for the greater part of both troubles, it should be remembered that the dust nuisance on a somewhat smaller scale existed long before its advent. If it has resulted in an awakened interest in this problem alone, it will have served a valuable purpose, but besides this it has exerted a beneficial influence in arousing the public at large to the knowledge that good roads are necessary to the welfare of any community, and thus has been instrumental in the construction of many miles of road which would otherwise have remained unbuilt. Bad roads are almost as injurious to the automobile as the automobile is to the road itself, so that the development of a practical road which will withstand its destructive action is a matter for coöperation between the automobilist, the road engineer and the general public.

Methods of Preventing Dust and Preserving Roads.— Many methods of solving the problems of dust prevention and road preservation have been suggested and tried, and while a large proportion have in themselves proved unsatisfactory, much valuable information has been obtained. There is probably no one solution that will meet all cases and it is only by considering the collective results of those who have experimented along these lines that a proper appreciation of the great number of factors which bear upon the subject can be obtained.

In regard to the dust problem alone there would seem to be three general ways in which it might be solved: (1) by the sanitary removal of dust from road surfaces, (2) by the retention of dust on the road surface, and (3) by the prevention of dust formation.

The first of these methods is usually followed in the case of city pavements and involves sprinkling the street with water and removing the moistened dust by sweeping. This is an expensive procedure, calling for almost continuous labor and close attention and is clearly impracticable for country roads. While it is a most useful and necessary method for the class of

pavements found in cities and towns, it is unsuited for roads which are either composed entirely of fine material or are dependent upon the retention of fine material upon their surfaces. Even for pavements the method as outlined above can sometimes be modified for the better, as will be shown later.

The retention of dust upon road surfaces may be brought about in either one of two ways or by a combination of both. The first lies in the control of those forces which tend to remove dust and the second by treatment of the surface dust with a view toward making it less susceptible to their influences. In regard to the natural forces which tend to remove dust, *i.e.*, wind and running water, it would seem that natural agencies might in many instances be employed to counteract them.

It is a well-known fact that the presence of trees mitigates the harshness of weather conditions in their immediate vicinity. As these conditions have an important effect upon a road, it is often possible by the proper maintenance of trees and hedges along a roadside to prevent much of the dust from being removed. Thus, shade trees will keep a road for a considerable time in a moist or semi-moist condition after a rainfall and materially aid in the laying of dust. At the same time, both trees and hedges protect a road from the full sweep of winds and therefore prevent, to some extent, the removal of dust by this means. Proper sodding and care of embankments along a road will also often reduce the formation of dust, by preventing the mechanical transportation of extraneous fine material to the road surface, and retard or prevent the removal of much fine material by running water.

With respect to overcoming the dust raising effect of automobiles, it would seem that regulations restricting the speed of such vehicles would, if enforced, be at least a partial solution of the problem, as the amount of dust raised is proportional to the speed at which the machine is driven. The demand for rapid transportation has, however, become so general that very severe restrictions cannot well be imposed, although excessive speeds should certainly be forbidden, except upon roads

especially adapted to very rapid traffic. In some instances, mainly in city and suburban parks, the problem has been met by forbidding the passage of automobiles over the roads, but this is certainly an unsatisfactory solution of the difficulty as the automobile is not only a thing of the present but of the future as well, and cannot be thus easily disposed of.

The automobilist himself has attempted to solve the dust problem to some extent, and in coöperation with the automobile manufacturer has demonstrated a number of valuable facts which, however, have not been followed up to the best advantage. During the summer of 1907 the Royal Automobile Club, of England, instituted a series of motor dust trials with a view toward finding, if possible, some method of overcoming the dust raising tendency of motor cars, by means of mechanical devices. A day was selected for observing the effect of the various machines traveling over a dust lain track with just sufficient breeze to move the dust raised by each car, but not enough to create such a dust cloud. It was very difficult to distinguish much difference in the character of the dust cloud raised by different cars, although those fitted with bodies high from the ground or else very low raised less dust than the average. Several novel devices were tried with more or less success. One of these which gave fairly good results was a machine made with a body high from the ground and fitted with an under shield and cased wheels. The best results were obtained with a car carrying a flat steel bottom under body, with sides overlapping the sides of the car, and shoes instead of mud guards. The under screen was only six inches from the ground, and projected beyond the radiator in front so as to catch the deflected wind from the face of the car and pass it between the screen and the car instead of between the car and the road. This car raised very little dust at a speed of thirty miles per hour.

The surface treatment of roads with a view toward making them less susceptible to dust raising forces has undoubtedly received more attention than any other one method of overcoming the dust nuisance. The materials employed in such treatment are known as dust palliatives and will be fully treated of in later chapters. For the present it will be sufficient to say that they are for the most part temporary binding mediums which moisten and hold the dust particles together and to the surface of the road. Water is the best known and most generally used material for this purpose, although perhaps the least satisfactory except when employed immediately before the road is to be cleaned. Numerous chemical substances especially manufactured for this purpose, as well as chemical byproducts, have also been used with more or less success according to their manner of application and the local conditions which they have had to meet.

The retention of dust upon the road surface by any of the means described above tends in a measure to solve the problem of road preservation by forming a cushion coat which protects the underlying road from wear, and in the case of broken stone roads acts as a binder for the coarser fragments. If, however, too much dust is retained by the road a disagreeable surface condition is produced, especially in wet weather when the dust becomes mud. This fact naturally leads to a consideration of means for preventing excessive dust formation, which is the third solution of the dust problem as outlined.

Prevention of dust formation means, according to our definition of dust, prevention of wear, and it is therefore a direct method of road preservation. Dust from outside sources will, however, always be encountered and when excessive will have to be dealt with according to one or more of the methods described under the first two headings. That is, even on roads where the products of wear are reduced to a mimimum by measures taken to prevent dust formation, the road may become dusty from outside sources and this dust should either be removed or retained upon the road surface by some suitable means. The latter method is seldom advisable except when employed merely to keep down the dust until it can be removed in a sanitary manner.

The first method which may be mentioned of preventing

dust formation on roads is the use of wide tires or rubber tires on horse drawn vehicles in place of the ordinary narrow steel tire. It is a well-known fact that the narrow steel tire under heavy loads cuts into the less resistant types of roads, forming deep ruts which soon fill with water and serve as starting points for excessive wear, even by rubber tired vehicles. Regulations against excessive speed of motor cars undoubtedly tend to preserve the roads from their destructive action as well as to prevent the removal of dust, as the damage caused by such machines increases with their weight and speed. The use of chains and other metal anti-skidding devices should also be forbidden, for practically no form of country road can successfully withstand their wear and tear, even if the road has previously been treated with a dust preventive or road binder. The avoidance of sharp curves in laying out new roads will also be an aid to road preservation, as the greatest damage from skidding is apparent at such places.

One solution of the problem which has been seriously considered by some road engineers is the construction of special automobile highways over which no other kind of traffic shall be allowed to pass. This would in many cases involve the construction of double highways, one side being reserved for horse drawn and the other for self-propelled vehicles. While such highways might have many desirable features, at the present time their construction involves too great an expenditure of money to be generally adopted. Where this plan has been carried out, however, the results have proved satisfactory.

For ordinary macadam roads the selection of a hard tough stone for the body of the road, and of good binding screenings for the surface, would undoubtedly improve the condition of many, but even the best of such roads will rapidly succumb to excessive automobile traffic. When only the softer kind of rocks are to be had, certain modifications of the customary form of macadam may be followed to advantage in increasing the resistance of the road to wear. Thus the use of the smaller sizes of crushed stone in the foundation course and of the larger

sizes in the wearing course will in some cases prove to be the best practice. To quote from a paper on this subject by A. N. Johnson:* "The fact that pieces of rock from two to three inches in size will lock or key together more firmly than one-inch size makes a surface composed of the larger sizes resist more effectively the action of automobile traffic. In many instances observed by the writer it has been noticed that the first place to give way has been where there evidently has been a cluster of finer particles." When employing a dust preventive or road binder with stone of poor wearing quality this form of construction can also undoubtedly be employed to advantage, with certain modifications which will be described in another place.

The construction of country roads similar to our city pavements would undoubtedly solve the problem of road preservation to a great extent, but unfortunately this is out of the question at the present time on account of cost. By approaching the city pavement form of construction as close as economy will permit, however, a long step will be taken in the right direction, and this fact will be appreciated as the subject of road binders is developed.

Careful maintenance is always a most necessary adjunct to preservation even of the most resistant forms of roads and pavements. This fact would seem to be so axiomatic as to hardly need discussion and yet in this country in particular the maintenance of roads is not given proper attention, and is often sadly neglected. This is not so often the fault of the engineer as of the people or controlling bodies who have to do with the appropriation of road funds. Among those who are not well informed on the subject the prevalent idea seems to be that a road once well built should last indefinitely, with little or no attention, except perhaps for a few slight repairs now and then. As a matter of fact this is far from being the case. All classes of roads and pavements require almost constant attention if

^{*} Specifications and Notes on Macadam Road Construction, Journal Western Society of Engineers, December, 1908.

they are to be kept in first class condition, and the expenditure of money for this purpose proves in the long run to be good economy. The European nations are considerably in advance of us in this respect and the sooner we follow their lead the better. This point cannot be urged too strongly in the case of roads treated with bituminous binders, for deterioration in the majority of such roads proceeds at a rapid rate when once begun.

The use of chemical road binders in the construction and maintenance of roads seems to be the most likely method of solving the problem of road preservation, and many experiments have been conducted along these lines by road engineers. great number of materials have been employed, various methods of application have been resorted to, and results of the most varied and seemingly conflicting character have been obtained. Enough has been accomplished, however, to show the possibilities of the use of chemical binders and the road engineer has come to regard them as his salvation. As in the case of dust palliatives, large industries have been developed for the purpose of supplying road binders of one kind or another and both classes of materials are now furnished by many manufacturers. In fact the differences between the two are, as will be shown later, often but differences in concentration of the same kind of binding base held by each.

Road binders are at present employed in two general ways: (1) in the surface treatment of roads and (2) in the internal treatment of roads. Their primary function is to bind the wearing fragments of the road together sufficiently to withstand the disrupting strains to which the road is likely to be subjected. They should also waterproof the road and thus minimize the effects of water and frost. A good road binder thus reduces wear and also dust formation. Some produce a rigid bond and others a more or less resilient bond. The latter are to be preferred for roads subjected to heavy horse drawn traffic as they lessen the effect of impact from the horses' shoes and of abrasion from steel tired wheels.

Road binders employed in the surface treatment of roads hold an intermediate position between the dust palliatives and the heavy internal binders. They are extensively employed in the treatment of old broken stone or gravel roads, while the latter are made use of in new construction work and in the resurfacing of old roads. Both the dust palliatives and road binders will be classified and described in later chapters and need not be further considered at this point, other than to state that they do not keep a road dustless for any great length of time, although they may reduce the formation of dust from the road material proper. Where dust formation from other sources is excessive the two classes should be employed conjunctively.

Necessity for Specific Information Concerning Dust Preventives and Road Binders. - Owing to the rapidity with which the production of dust preventives and road binders has developed and the great number of preparations now on the market, as well as to the discouraging and often misleading results obtained by their experimental use, the road engineer is frequently at a loss to decide upon just what material he should use and just how he should afterwards employ it to best advantage. The information which he has had to rely upon is for the most part that which he can obtain by reading reports of experiments which in many cases have been conducted under entirely different conditions from those with which he has to contend, or else from the descriptive circulars issued by manufacturers of these preparations. So many conflicting opinions are held by different parties who claim to be experts on the subject that their collective ideas serve only to confuse him unless he has the time and inclination to work out the problem for himself and separate the facts from the fallacies. To do this requires a certain amount of chemical knowledge, in which he is usually deficient, never before having been called upon to combine chemistry with road building. While it is true that the development of the paving industries has resulted in the accumulation of much data, both on the chemical and mechanical side of pavement construction, which is of unquestioned value in connection with modern road

work, the subjects of dust prevention and road preservation require somewhat different treatment. In other words the principles which have been established in the paving industry will often have to be modified and differently applied in considering the treatment and construction of roads with dust preventives and road binders. For example, the expensive paving materials and refinements of construction in building and maintaining city pavements cannot usually be employed in road work on account of cost, and recourse must, therefore, be had to cheaper materials and cheaper forms of construction which would not be considered good practice in the former case.

It is evident, therefore, that necessity exists for specific information relative to the chemical and physical characteristics of dust preventives and road binders, which will enable the road engineer to select and specify materials best suited to his needs, and also as to the best method of applying such materials. whole subject is at present in an undeveloped state and there is much vet to be learned, but certain fundamental facts have been demonstrated which, if generally understood, should do much toward putting matters on a firm footing and aid in clearing up the apparent contradictions which now exist. While the road engineer has been experimenting with various materials about which he knows little or nothing regarding their chemical and physical properties, the manufacturer of these products has also been experimenting on his own account both at the working expense of the engineer who has employed his material and at the financial expense of the public. As the subject is in its infancy this is of course only a natural procedure on the part of any progressive manufacturer who wishes to improve his product, but except to himself it has resulted in much confusion, owing to changes, of which the engineer knows nothing, made in products whose only recognized means of identification are their trade names. This fact has more than once come under the observation of the author both in laboratory and field work.

Another although somewhat similar cause of confusion lies in the great variations in composition of certain classes of materials known under very general names. Thus coal tars vary so among themselves that it is safe to say that no two tars obtained from different localities have the same composition, and in fact samples obtained from the same plant at different times will often show considerable variations in character.

How then, it may be asked, can the road engineer even identify materials which he has employed and how can he intelligently select and specify those materials which will give him the best results? These are the questions that would seem to be of paramount importance and which can be answered only by a careful review and digestion of all the reliable data to be obtained from both theory and practice. Without this knowledge work with dust preventives and road binders will be purely experimental and most experiments so made will continue to be as in the past of doubtful value both to the experimenter and those who should profit by his experiments.

The Future Road. — In connection with the problem of road preservation much discussion has arisen as to what form the future road will take. To the author's mind the most plausible answer to this question would seem to be some form of city pavement, probably of a bituminous nature. This, however, is a matter of the far distant future and will be accomplished only by a slow evolution of the modern macadam through the stages of a bituminous treated surface, a bituminous bound wearing course with ordinary macadam base, and a bituminous bound wearing course with cement concrete base. The macadam is at present passing through the first stage and while the second is within sight, some time will probably elapse before it is generally adopted.

In connection with the two methods mentioned above for treating roads with chemical road binders, *i.e.*, surface treatment and internal treatment, there are two problems connected with the preservation of roads. The first deals with the preservation of existing roads and the second with that of new roads which are being constructed. Until the old roads are sufficiently worn to require resurfacing, it is evident that

surface treatment is the most economical. In resurfacing or construction work, however, internal treatment can be employed to advantage. At present this is most generally accomplished by what is known as the penetration method, in which the wearing course is treated after being laid. As working facilities grow better and traffic conditions more severe this will be gradually superseded by the mixing method, in which the road stone constituting the wearing course is covered with the binding medium before being laid on the road. The first important step toward the city pavement form of construction will then have been taken, and the construction of a more rigid foundation by the use of an hydraulic cement will naturally follow, as will also other details of construction approaching that of the city pavement. In individual cases this development has already taken place, but, like men who are intellectually in advance of their time, they are not representative of the main portion.

The most direct cause of this evolution of the macadam road will be the continued rapid growth of automobile traffic and the adoption of the motor van for commercial transportation. Statistics show the following increase in number of motor vehicles manufactured in the United States during the years 1900 to 1909 and it is only reasonable to suppose that this is an indication of what the future rate of increase is apt to be.

APPROXIMATE PRODUCTION OF AUTOMOBILES IN THE UNITED STATES.

| Year. | Number. | Year. Number | |
|-------|---------|--------------|---------|
| 1900 | 4,192 | 1905 | 30,000 |
| 1901 | 10,000 | 1906 | 40,000 |
| 1902 | 15,000 | 1907 | 40,000 |
| 1903 | 19,400 | 1908 | 55,000 |
| 1904 | 25,000 | 1909 | 114,900 |

It is estimated that there were 40,000 motor vehicles in the United States at the close of 1902. What the number is at

present is problematical, but as the Census Report of 1908 shows that during 1907 and 1908 the number of automobiles exported amounted to 5339 against 2121 imported, it is evident that for the ten years enumerated above there was a comparatively small diminution in numbers, due to exports. The estimated total production since 1902 is 324,300 which added to the 40,000 above mentioned gives a grand total of 364,300. A large proportion, at least two-thirds, of these machines are probably in use in this country at the present time. During 1909 there were approximately 270 firms engaged in the manufacture of motor vehicles and about 125,000 men employed in the industry. The total value of the machines produced amounted to about \$135,000,000, for that year. A large increase in production is indicated for some years to come.

An increase in motor vans capable of carrying heavy loads is also an assured fact for economic reasons. It has been estimated that in England under favorable conditions the cost of haulage per ton mile for gasoline delivery vans lies between twelve cents for light loads and five to six cents for heavy loads. For the steam tractor, an innovation which has not yet been adopted in the United States, this figure is reduced to two and one-half cents per ton mile in comparison with six and one-half cents for horse drawn vehicles. In this country, where the price of gasoline is much cheaper, it is probable that even greater differences in favor of the motor vehicle will be shown as this form of traffic develops.

Owing to the exceedingly heavy loads which will sooner or later be transported over our roads in this way the necessity will arise for a more stable foundation than that of a newly constructed macadam road, and it would seem highly probable that the cement grouted foundation will be the one to be employed. If motor traffic alone were to be considered, a road built entirely of cement concrete might prove the most satisfactory and economical form for the future. For mixed traffic, however, such a road is by no means ideal and as, in spite of the increase in motor vehicles, the number of horse drawn vehicles

does not seem to be decreasing, a form of road best suited to meet the requirements of both classes of traffic will have to be considered. The type of road with cement concrete foundation and bituminous concrete surface as described above would, therefore, seem in the light of our present knowledge to be best suited to meet these requirements. It is, of course, possible that new materials of construction will be discovered or invented which will prove more satisfactory, but at the present time there are no indications that this will happen.

Summary and Conclusions. — In this chapter the problems of dust prevention and road preservation have been considered in detail and their causes and effects studied. The relations between the two problems have been discussed and also methods of solving them. The importance of the dust problem has been shown by a consideration of the undesirable effects of road dust upon public health and comfort, upon personal and real property, upon vegetation of all kinds and upon the road itself.

The causes of road dust formation are the chemical, physical and mechanical agencies which produce wear of the road, and the transportation of extraneous fine material to the road surface from outside sources. As road dust is largely a product of road wear it is evident that the problems of dust prevention and road preservation are closely associated.

The most important dust raising and road destroying factor of modern times is the fast moving motor car, owing to air currents generated in its rear and to the great tractive force exerted by its rear wheels upon the road surface. Any solution of the two problems must, therefore, deal largely with methods designed to overcome these tendencies of the automobile, although the effect of impact and abrasion of ordinary traffic must also be considered, and especially the combined effect of both classes of traffic.

There are three general methods of reducing dust formation which should be considered in attempting a solution of this problem: (1) by the sanitary removal of dust from road surfaces: (2) by the retention of dust upon the road surface, and (3) by

the prevention of dust formation. Any or all of these methods may be employed to solve the problem of road preservation. The most promising solution would seem to lie in the treatment of roads with chemical substances known as dust preventives and road binders, which may be applied to the surface or in the body of the road according to circumstances. The importance of other methods described should, however, never be lost sight of, for it is only by a combination of methods that the two problems can be successfully solved.

The necessity for specific information on the part of the road engineer concerning the composition and properties of chemical dust preventives and road binders as related to their use, has been discussed and it has been stated that many experimental failures and much confusion as to the cause of such failures are directly attributable to this lack of knowledge.

In conclusion the most probable form of road which will be developed in the future has been considered, and it has been shown that indications point toward the evolution of the modern broken stone road to one having a cement concrete base and a bituminous concrete surface.

CHAPTER II.

CLASSIFICATION OF DUST PREVENTIVES AND ROAD BINDERS.

Dust preventives may be conveniently classified in two ways, *i.e.*, according to the purpose for which they are used, which depends to a great extent upon their physical properties, or according to their chemical composition. A combination of both classifications is probably the most satisfactory way of considering them, and this course will be pursued in the following chapter, when individual materials are discussed. Before doing this, however, it may be well to briefly describe each method separately.

Classification According to Purpose for Which Used. - In this classification the names dust preventives and road binders at once suggest two divisions. It has been stated that dust preventives or palliatives may be considered as temporary binding mediums for dust particles, and road binders as more or less permanent binding mediums employed for the purpose of holding together the mineral fragments constituting the body or at least the surface of the road. Such materials may be applied either to the finished surface or internally to the road during construction or resurfacing. In the former case, as would naturally be expected, the results are of a less lasting character than in the latter. Binders applied to the surface will of course disappear more or less rapidly according to their depth of penetration, as the road surface wears down, while those applied in the construction of roads should prove effective as long as the road itself lasts or until the wearing surface is destroyed. They may, therefore, be considered as semi-permanent or permanent compared with the dust palliatives or temporary binders. Three main classes are thus established, although no sharply defined lines can be drawn between them, owing to the fact that some materials merge from one class into

another according to their inherent properties or to the quantity that is applied at any one time. The degree of concentration of the binding base contained may also cause certain materials to be classified under more than one heading. For all practical purposes, however, the classification mentioned above will be followed and this method may be used as a sub-classification when arranging the materials according to their chemical composition. We may, therefore, consider dust preventives and road binders as being either:

- (1) Temporary binders.
- (2) Semi-permanent binders.
- (3) Permanent binders.

Temporary Binders. — The temporary binders are for the most part applied to road surfaces solely for the purpose of laying dust, both that produced from the road itself and that brought in from outside sources. By thus keeping a film or layer of fine material upon the road surface they may also tend to preserve the under surface of the road from wear and in the case of broken stone roads from the disintegration which would result from the removal of fine material from the interstices between the coarser fragments of the wearing surface. On roads and pavements that are frequently cleaned they are ordinarily employed to lay the dust just before cleaning, in order that it may be removed without being dispersed into the atmosphere. The temporary binders from their very nature must be applied at frequent intervals, sometimes as often as two or three times a day, and sometimes at periods varying from one to four weeks.

In order that they may be employed at all, it is, for reasons of economy, necessary that they be capable of easy application. The only economical method of applying such materials is by means of a sprinkling cart and they must, therefore, be thin liquids, viscous liquids miscible with water, or solids readily soluble in water. Their power of holding the dust particles together may be due to one of two properties, that of capillary attraction

or to the presence of a certain amount of true binding base. In the first case they simply moisten the surface of the particles which are then held together by the capillary attraction of the films of liquid between them. In the second case the particles are actually cemented together by films of sticky or glue-like materials. In certain rather exceptional cases, temporary binders may react chemically with the fine mineral fragments of the road to produce binding films of a colloid or glue-like character. Their dust laying effect is of short duration because of the fact that they either volatilize readily, are carried away by rains, or soon become saturated with dust, thus being rendered incapable of holding down fresh dust which may be formed or brought upon the road. Those that do not volatilize and are of an inherently sticky nature, if insoluble in water, concentrate upon the road surface after a number of applications and thus become in effect semi-permanent binders. This is the most valuable type of dust palliative for use on roads which are not cleaned frequently.

The temporary binders are employed mainly on city, park and suburban roads where dust from outside sources has to be taken care of, and are often used in conjunction with the other classes of binders. As has been said they are applied by means of a sprinkling cart in the same way that water is applied. No definite rules can be laid down in regard to the frequency with which they should be employed, as this is not only dependent upon the physical properties of each material, but also upon the local conditions to which the road is subjected. This subject will be discussed elsewhere at greater length.

Semi-Permanent Binders. — The semi-permanent binders are applied to road surfaces mainly for the purpose of preserving the road from wear, although they also serve as dust layers for some time after application, and, of course, prevent excessive dust formation from the materials of which the road is composed. Their property of laying dust, especially that from outside sources, is limited by their capacity for absorbing the dust. A single application of these materials should preserve

the road surface from disintegration and appreciably lessen dust formation for a period of at least one year. They cannot, however, be expected to keep a road dustless for this length of time where any considerable quantity of dust from outside sources is encountered.

The semi-permanent binders are liquids containing appreciable quantities of true binding materials and are applied cold or hot according to their viscosity at ordinary temperatures. If sufficiently fluid to apply cold, certain of their constituents should be of a rather volatile nature, or else show a tendency to harden upon exposure. In the former case, ease of application is obtained at the expense of the material lost by volatilization, the true binding base being merely diluted by the volatile constituents, and left upon the road after they have disappeared.

Cold applications may usually be made by means of an ordinary sprinkling cart, but hot applications require hand labor or else especially constructed sprinkling contrivances. Distributing carts carrying spraying devices and so equipped that the material may be heated in the cart and forced upon the road surface under air or steam pressure are extensively employed in England and France. A number of these machines have been imported to this country and are now being used in the surface treatment of roads.

As the semi-permanent binders seldom prove effective for over a year, they may best be applied in the early spring at the beginning of the dusty season. They rarely withstand the severities of winter weather and winter traffic, and unless applied at the time mentioned are not apt to give satisfactory results for even a year. They must of course be applied annually but never to a worn-out or badly rutted surface. In most cases it is desirable and in some absolutely necessary to remove all loose dust and detritus from the road surface before applying them, and any repairs required should be made before application. These materials give best results on broken stone or gravel roads which are not subjected to exceedingly severe traffic conditions,

but which require some medium to consolidate and hold down their wearing surface. Some of them have been employed in the treatment of earth roads, but it is usually better practice to reconstruct such roads with the addition of a suitable permanent binder, which will add to their stability.

Permanent Binders. — Permanent binders are employed in the construction of roads and pavements primarily for the purpose of holding the coarser wearing particles together. By preventing disintegration and reducing wear they also reduce dust formation from the road material itself. They are heavy binding mediums adding to the stability of the road but having little absorptive capacity for dust. They should prove effective until the wearing surface of the road is actually worn out.

Such binders include the very viscous or semi-solid bituminous cements which produce a well-bound resilient concrete when incorporated in a mineral aggregate, and mineral cements which produce a rigid concrete. The former reduce wear through the cushioning effect which they exert upon the wearing fragments, while the latter actually take up a considerable amount of wear themselves and are effective because of the hardness and density of the concrete which they produce. Bituminous cements are employed in the construction of nearly all classes of roads and pavements, while mineral cements are almost exclusively employed in pavement work. Either type of material may be used throughout the entire depth of road or only in the wearing surface. Both can often be employed to advantage in the same road, and when this is the case the mineral cement is usually worked into the foundation and the bituminous cement into the wearing surface.

Permanent binders may be applied to the road proper while under construction, or they may be mixed with the road material before being laid. Either method may be carried out by hand or mechanical labor. Bituminous cements, unless containing large quantities of volatile materials, should be of such consistency as to require heating before being applied and it is often desirable to heat the mineral aggregate before they are incor-

porated with it. This, however, is only done when the mixing method is followed. Permanent binders are employed to best advantage on highways subjected to rather severe traffic conditions and their use should always be supplemented by that of a temporary binder or dust palliative where outside dust is excessive.

Classification According to Chemical Characteristics.—Bearing in mind the explanations given above as to what is meant by the terms temporary, semipermanent and permanent binders, and the brief descriptions of the various physical properties of these three classes of materials as regards their use, we may take up their further classification according to chemical characteristics. This is a purely arbitrary matter depending upon the point of view of the classifier. For a number of reasons it has seemed best to the author to consider dust preventives and road binders under two broad headings and to divide each of these divisions into two general subdivisions as follows:

- I. Non-bituminous materials.
 - (a) Inorganic.
 - (b) Organic.
- II. Bituminous materials.
 - (a) Petroleums, petroleum products and solid native bitumens.
 - (b) Tars and tar products.

The convenience of this method of classification will become apparent as the subject is developed. Each of the subdivisions may now be considered under the headings temporary, semi-permanent and permanent binders.

Inorganic Materials. — Chemically speaking, inorganic substances are differentiated from organic by the fact that the carbon atom is either absent from their molecules or else exists in such a state of combination that the material cannot be considered as a hydrocarbon or hydrocarbon derivative. Thus water, whose chemical symbol is H_2O , and common salt (NaCl) contain no carbon atom in their molecules and are, therefore, inorganic materials. On the other hand limestone or calcium

carbonate (CaCO₃), while containing a carbon atom, cannot be considered as a hydrocarbon derivative and is also classified as inorganic.

Among the temporary binders water is the first substance which should be mentioned. Solutions of such chemical salts as calcium chloride and magnesium chloride whose hygroscopic properties are made use of for the purpose of increasing the dust laying efficiency of water come next in order. There seem to be no semipermanent binders among the inorganic materials unless solutions of salts, which are supposed to react with each other or with the fine mineral particles upon the road surface to form colloidal binding films, may be so considered. Such materials have not been employed to a sufficient extent to warrant any very definite opinion as to which of the two classes they should belong. Sodium silicate solutions alone or employed in connection with water soluble salts of calcium and magnesium may be taken as typical of this class of materials.

The permanent inorganic binders are the various hydraulic cements which produce hard and rigid concretes. Among them may be mentioned natural cements, Portland cements and slag cements. They are the most powerful known road binders, and when employed in considerable quantity produce with the mineral fragments of the road a true monolithic surface. This is an important characteristic which effects the results obtained by their use as compared to those obtained from the use of the heavy bituminous cements.

Non-Bituminous Organic Materials.— Among the temporary binders of this division may be mentioned such vegetable oils as oil of aloes whose dust laying properties are similar to those of water. That is, they contain little or no true binding base but hold the dust particles together through capillary attraction. Being of a less volatile nature than water one application will keep down the dust for a much longer time. In common with most poor binding oils they have certain undesirable properties which will be discussed in Chapter V. Animal fats such as waste grease obtained from wool scourings may be considered as

temporary binders and show the same general characteristics in so far as road treatment is concerned. Some of these materials are applied in their natural condition but more often in combination with other materials in the form of emulsions. They are mainly employed in patented road preparations.

As an example of the semipermanent binders may be mentioned concentrated waste sulphite liquors, obtained and prepared from the waste products produced in the manufacture of wood pulp according to the sulphite process. Waste molasses residues when combined with quicklime may also be noted among this class of materials. These substances either contain an appreciable amount of true binding base or are inherently sticky liquids. Most of them are somewhat soluble in water and cannot, therefore, be employed as permanent binders without the addition of a waterproofing agent, no matter how powerfully they bind the mineral fragments of the road together. With the exception of the two mentioned and possibly a few others, they are of interest only because they have been suggested for road work and not because they have been employed for this purpose to any extent.

At the present time there would seem to be no non-bituminous organic materials which might be considered as permanent binders, except perhaps compounds of rosin with certain inorganic bases, which will be described in their place.

Petroleums, Petroleum Products and Solid Native Bitumens.— As the greater part of this book will be devoted to a consideration of bituminous road materials, it is unnecessary in this chapter to do more than note representative types of the subdivisions of the classification described.

The temporary binders may be represented by crude paraffin petroleums, petroleum distillates and semiasphaltic and asphaltic oil emulsions. The first two materials like the vegetable oils show little or no true binding properties but are dependent upon their moistening property to keep down the dust particles. They are essentially lubricants and when present in any considerable amount are apt to disintegrate the road surface rather than

bond it. A better class of temporary binders is found in the asphaltic oil emulsions which often prove to be excellent road preservatives.

Semipermanent binders may be represented by the heavy semiasphaltic and asphaltic petroleums and the liquid residuums obtained from such oils. According to their viscosity, percentage of volatile oils and asphaltic contents they merge gradually into the permanent binder class.

Semisolid and very viscous asphaltic and semiasphaltic oil residuums, as well as native asphalts and solid native bitumens of an asphaltic character, make up the permanent binder class. The two former are the most commonly employed in road construction and the two latter in city pavements. Of late, however, both the asphalts and other solid native bitumens when cut with comparatively large amounts of oil fluxes have been used to some extent in road work. Such mixtures exhibit properties quite similar to the heavy asphaltic oil residuums.

Tars and Tar Products. — These materials include the tarry liquids produced from the destructive distillation of bituminous coal and petroleum oils, and their refined products. Many other materials such as wood, bone, etc., when subjected to this process produce artificial bitumens known as tars but as these are seldom if ever employed as dust preventives or road binders, they will be given but passing notice.

Among the temporary binders of this class may be mentioned tar distillates, such as creosote oils, very watery crude tars, such as oil gas or water gas tar, and tar emulsions. Tar distillates and the crude watery tars may be compared to the petroleum distillates and crude paraffin petroleums, and the tar emulsions with the semiasphaltic and asphaltic oil emulsions so far as their dust laying and road binding properties are concerned. From a chemical standpoint, however, they are quite different.

The heavier crude tars and partially refined or fluid tar residuums may be considered as semipermanent binders and are comparable with the crude asphaltic oils and fluid oil residuums. They also merge gradually into the permanent binders, according to their viscosity and relative volatile oil and pitch contents.

The permanent binders of this class of materials comprise the very viscous and semisolid pitch residues obtained from fractional distillation of the crude tars. Such products are entirely analogous to the heavy oil residuums and oil pitches mentioned under the natural bitumens. Tar pitches, like asphalts, have been employed to a considerable extent in the construction of city pavements.

Summary and Conclusions. — In this chapter the classification of dust preventives according to their use and chemical characteristics has been described. The two methods of classification have been combined and representative types of materials have been noted. Temporary binders are those which are intended to be applied at frequent intervals; semipermanent binders are materials which upon one application prove effective for approximately one year or at least throughout a dusty season; and permanent binders are those which last as long as the wearing surface of the road remains intact. Materials holding intermediate positions also occur so that this division is not a sharp one.

For the sake of reference this classification is given below in tabular form. In this table it has not been considered necessary to include all known dust preventives and road binders, and only the most important or representative types have, therefore, been given:—

CLASSIFICATION OF DUST PREVENTIVES AND ROAD BINDERS.

- I. Non-bituminous materials.
 - (1) Inorganic.
 - (a) Water.

Calcium chloride and other hygroscopic salts.

- (b) Sodium silicate and other chemicals capable of reacting with each other or with the road fragments to form colloidal binding films.
 - Rock and slag powders.
- (c) Portland and other hydraulic cements.

(2) Organic.

- (a) Oil of aloes and other vegetable oils.Wool scourings and other animal greases.
- (b) Concentrated waste sulphite liquors. Waste molasses residues.
- (c) Resinates.

II. Bituminous materials.

- (1) Petroleums, petroleum products and solid native bitumens.
 - (a) Crude paraffin petroleums.Petroleum distillates.Semiasphaltic and asphaltic oil emulsions.
 - (b) Viscous crude semiasphaltic and asphaltic petroleums. Liquid semiasphaltic and asphaltic oil residuums.
 - (c) Very viscous and semisolid semiasphaltic and asphaltic oil residuums or oil pitches. Asphalts and other solid native bitumens of an asphaltic nature.
- (2) Tars and tar products.
 - (a) Crude water gas tars or oil gas tars.Tar oils or distillates.Emulsions containing tar.
 - (b) Crude coal tars. Liquid tar residuums.
 - (c) Very viscous tar residuums. Tar pitches.

In conclusion it may be well to mention the fact that dust preventives and road binders as found upon the market do not always consist of one class of materials but may be mixtures of two or more classes. They may also have been chemically treated in various ways so as to modify or alter their original properties. Such preparations cannot well be classified under any one of the headings given above and it is often an exceedingly difficult matter to determine just what the preparation is composed of. Thus an asphalt or other solid native bitumen may

have been fluxed with an oil residuum or a refined tar in such a manner as to conceal its identity and various other deceptive combinations may be encountered. Certain methods of examination have, however, been devised which are of great assistance in identifying and classifying such materials and these methods will be described later.

CHAPTER III.

INORGANIC DUST PREVENTIVES AND ROAD BINDERS.

As has been stated in Chapter II, non-bituminous dust preventives and road binders may be divided into two main classes, inorganic and organic. In this chapter and the next the individual materials composing the first class will be taken up and discussed, according to their arrangement as previously given. It has seemed well to the author to also include the methods of application and relative value of these substances in order to prepare the way for the exclusive consideration of bituminous materials in the succeeding chapters. By so doing, much confusion will be avoided and a better idea of the entire subject will be obtained than if they are considered together.

Water. — Water is undoubtedly the first material ever used for the purpose of laying dust, and in cities and thickly settled suburban districts is at present the most generally employed. During hot dry weather its use has seldom proved satisfactory, owing to its rapid evaporation. Frequent and heavy applications are often required to keep the dust down and in many localities where traffic is heavy, it is practically impossible to obtain good results by the use of water alone. The cost of frequent sprinklings with water is a considerable item; and when the fact is taken into account that at the end of a season but little permanent benefit has been derived from its use, it will be seen that dust laying by this method is by no means economical. too heavy applications are made to broken stone roads the surface is apt to be gullied, and the dust converted for the time being into mud. As has been stated, the principal value of water in laying dust consists in the mechanical bond produced by force of capillarity when two wet surfaces are brought in contact. In proper quantities its presence is necessary to preserve the

cementing power of the fine particles of ordinary broken stone roads, and it often reacts with such particles to form colloidal or crystalline binding materials which hold the road surface in place. It will not, however, produce this effect upon all kinds of rock dust, and this fact has been made the basis of methods for determining the relative cementing value of different rock powders.

A practical physical test for determining the cementing value was first developed by Page, working in coöperation with the Massachusetts State Highway Commission, and further under Page and Cushman in the Division of Tests, Bureau of Chemistry, U. S. Department of Agriculture, and later in the laboratories of the U. S. Office of Public Roads. The underlying reasons for the cementing value of rock dusts and the curious variations that are noted in this property were developed in the exhaustive researches of Cushman extending over a number of years. For the fullest information with regard to this subject the original papers * should be referred to.

Water is ordinarily applied by means of horse drawn sprinkling carts although self-propelled sprinklers have also been employed to some extent. These carts vary in capacity from 300 to 1000 gallons and over. The water should preferably be distributed in the form of a spray and not forced directly upon

* "On the Cause of the Cementing Values of Rock Powders and the Plasticity of Clays," A. S. Cushman, J. Am. Chem. Soc., 1903, Vol. XXV, No. 5, pp. 451–468.

"The Testing of Road Materials," L. W. Page and A. S. Cushman, Bull. 79, Bureau of Chemistry, U. S. Dept. Agriculture.

"The Colloid Theory of Plasticity," A. S. Cushman, Trans. Am. Ceramic Soc., 1904, Vol. VI, pp. 3–16.

"The Useful Properties of Clays," A. S. Cushman, Circ. 17, Bureau of Chemistry, U. S. Dept. Agriculture.

"The Cementing Power of Road Materials," L. W. Page and A. S. Cushman, Bull. 85, Bureau of Chemistry, U. S. Dept. Agriculture.

"The Effect of Water on Rock Powders," A. S. Cushman, Bull. 92, Bureau of Chemistry, U. S. Dept. Agriculture.

"A Study of Rock Decomposition Under the Action of Water," A. S. Cushman, Circ. 38, Office of Public Roads, U. S. Dept. Agriculture.

"The Development of the Test for the Cementing Value of Road Material." A. S. Cushman, Proc. Am. Soc. for Test. Mat., 1906, Vol. VI, pp. 525-531.

the road surface. The use of a sprinkling device discharging the water through an adjustable slot so arranged as to force it from the valves at an angle inclined above a horizontal plane is one of the best methods of accomplishing this. Any such device should always be under the control of the driver, so that the volume of water discharged may be easily regulated. The quantity of water necessary for one application will vary with the character of the road surface treated, more being required for absorbent surfaces than for those which are impervious or nearly so. From 0.3 to 0.5 gallon per square yard may, however, be taken as an average. The frequency of application will also vary according to local conditions, such as character of the road, climatic conditions, amount of traffic, etc. In some instances it has been found necessary to sprinkle a road as often as three or four times a day and even then the dust has not been successfully laid.

The cost of laying dust by means of water is impossible to estimate, except in individual cases, being dependent not only upon the quantity required and frequency of application, but also upon the cost of the water itself, price of labor, efficiency of labor and availability of the water supply. The last factor alone makes it impossible to water the average country road, which is not equipped with the wayside hydrants necessary to carry on such treatment.

Aitkins * states that "The cost of ordinary sprinkling with water is generally about 4 s. per mile of road eight yards wide. The number of applications varies considerably but may be taken at about three hundred each year (two and one quarter times each day during the season), at a cost of £60 per mile per annum." This figures out to about two and one-quarter cents per square yard per annum. In the United States, figures obtained from various sources show that where any serious attempt is made to keep down the dust for a season by means of water sprinkling, this cost has averaged from two and one-half to five cents per square yard per annum. This represents an annual expenditure

^{* &}quot;Road Making and Maintenance," Second Edition, p. 328. Griffin and Co.

of from \$220 to \$440 per mile of fifteen foot roadway. In many cases the actual cost has been greatly in excess of the figures given.

Sea Water. — It has long been known that certain salts have so great an affinity for water that they are not only capable of retaining moisture for a long time under conditions which would otherwise produce rapid evaporation, but that they are capable of absorbing water from the atmosphere to a great extent. Some of these salts are so hygroscopic that in a humid atmosphere they will often completely dissolve in the water which they have absorbed from the air. Salts of this character are termed deliquescent, and it is to a great extent these hygroscopic and deliquescent salts that have been employed as dust preventives. Their chemical action upon certain rock powders may also increase the formation of binding material to some extent, but they are not primarily employed for this purpose. Their principal use is to keep the road surface in a semimoist condition for a much longer period than would be possible by the application of a corresponding amount of water only, and the number of sprinklings necessary is therefore greatly reduced.

One of these salts, magnesium chloride (MgCl₂), occurs to a considerable extent in sea water. The effect of its presence in the cheaper grades of table salt may be seen in the tendency exhibited by the salt to clump in damp weather. This is due to the absorption of water by the small amount of magnesium chloride which remains even after the salt has been purified. On account of the presence of this substance, sea water has been tried, in a number of favorably situated localities, for the purpose of laying dust. While the number of sprinklings has been somewhat reduced by this means, the results have, as a rule, been far from satisfactory, owing to the presence of an excessive amount of common salt (sodium chloride), which is applied at the same time and which has no hygroscopic properties. extremely dry weather, a hard salty scale is produced on the road which is very undesirable and in wet weather the mud contains so much salt that it is injurious to the varnish and iron work on vehicles. This strong salt mud is also apt to cause soreness around the fetlocks of horses.

Bittern. — In the process of manufacturing ordinary salt from sea water or other brines, a waste product is obtained which is known as bitter brine, or bittern. This bittern is the mother liquor remaining after most of the sodium chloride has been crystallized out by evaporation. It is comparatively rich in magnesium chloride, and, therefore, more suitable for road use than ordinary sea water. It also contains varying amounts of calcium chloride, calcium sulphate and other salts. As it is worthless for other purposes, its cost is very low and in certain localities its use might prove economical. Its application for the purpose of laying dust is covered by patent.* So far, no very extensive use has been made of this substance, but, as it is apt to contain a considerable amount of inert sodium chloride, the same objections which have been urged against the use of sea water might be applicable here, although to a much less extent. It undoubtedly has greater dust-laying qualities than ordinary sea water, but not so much as the salt which will next be considered, calcium chloride.

Calcium Chloride. — Calcium chloride (CaCl₂) is one of the most hygroscopic and readily deliquescent salts known, and should not be confused with the commercial product, commonly known as chloride of lime or bleaching powder, which has the formula CaOCl₂ and is employed as a bleaching agent and disinfectant. From very concentrated solutions calcium chloride crystallizes with six molecules of water, CaCl₂. 6 H₂O. At 30° C. these crystals melt or rather dissolve in their own water of crystallization and this fact makes calcium chloride more serviceable for dust laying than magnesium chloride. The latter also crystallizes with six molecules of water and while in humid air such crystals appear to be as hygroscopic as the former, they are more stable, and do not dissolve in their own water of crystallization at ordinary temperatures. This means that under certain conditions when calcium chloride would remain in liquid

^{*} U. S. Patent No. 828,643, Aug. 14, 1906.

form upon a road, magnesium chloride would exist as a solid and would, therefore, be less efficient as a dust layer. The comparative water absorbing capacity of these two salts in a humid atmosphere under normal summer conditions is shown by the following experiment, which at the same time demonstrates the remarkable affinity which both have for atmospheric moisture.

In this experiment separate solutions of the salts were first made and their actual salt contents determined by analysis. Known quantities of these solutions were then measured into weighed platinum dishes and placed in a hot air bath at 95° C. for two and one-half hours. The dishes and contents were then cooled and weighed and the loss in weight upon the basis of salt present determined, after which they were replaced in the oven at a temperature of 95° C. for an additional seven hours and their loss in weight again determined. At this point the contents of both dishes were solid. The salts were next exposed to air under normal conditions for varying periods and the percentage gain in weight due to moisture absorbed from the atmosphere noted. The results as given in the following table are calculated upon both a weight and molecular equivalent basis for the purpose of comparison.

RELATIVE HYGROSCOPICITY OF CALCIUM AND MAGNESIUM CHLORIDES.

| 40 Per cent Solution of Crystals having 6 $\mathrm{H}_2\mathrm{O}$. | CaCl ₂ . | | $\mathrm{MgCl}_2.$ | |
|--|-------------------------------|---|----------------------------|--|
| | Per cent H ₂ O. | $\begin{array}{c} \text{Molecules} \\ \text{H_2O} \\ \text{per Mol.} \\ \text{Salt.} \end{array}$ | Per cent H ₂ O. | $\begin{array}{c} \text{Molecules} \\ \text{H}_2\text{O} \\ \text{per Mol.} \\ \text{Salt.} \end{array}$ |
| Solution heated for 2½ hours at 95° C | 206.5 | 12.7 | 218.0 | 11.5 |
| Solution heated for 9½ hours at 95° C | 62.2 | 3.8 | 108.3 | 5 · 7 |
| Residue exposed to normal atmospheric conditions, 24 hours | 104.7 | 6.2 | 138.1 | 7 · 3 |
| conditions, 48 hours | 144.3 | 8.9 | 168.4 | 8.9 |
| conditions, 72 hours | 169.9 | 10.5 | 191.3 | 10.1 |
| Residue exposed to normal atmospheric conditions, 89 hours | 198.5 | 12.2 | 219.0 | 11.6 |
| conditions, 96 hours | 186.3 | 11.5 | 204.3 | 10.8 |
| Residue exposed to normal atmospheric conditions, 113 hours | 184.7 | 11.4 | 202.8 | 10.7 |

From these figures it will be seen that weight for weight magnesium chloride holds a greater percentage of water than calcium chloride, under the same conditions. This is true of all of the results but it will be noticed that at the point of maximum absorption one molecule of calcium chloride is capable of absorbing and holding a greater number of molecules of water than one molecule of magnesium chloride. The molecular absorption is, therefore, higher for the former and this, in connection with the fact that at ordinary temperatures CaCl_2 . 6 H_2O is a liquid while MgCl₂. 6 H_2O is a solid, makes calcium chloride chemically more efficient as a dust layer then magnesium chloride.

When carrying out these experiments it was noticed that under working conditions the calcium chloride did not become solid until all but four molecules of water were removed from one molecule of CaCl₂. Magnesium chloride, on the other hand, became solid while still retaining six molecules of water to each molecule of MgCl₂. From the standpoint of the solid state, therefore, the maximum efficiency as shown by the experiment would be as follows, and these figures undoubtedly represent more nearly the relative dust laying efficiency of the two materials:

| Residue Exposed 89 Hours. | CaCl ₂ . 4 H ₂ O. | MgCl ₂ . 6 H ₂ O. |
|---------------------------------|---|---|
| Per cent water held as moisture | 80.7 8.2 | 49.6 |

Viewed in this light solid calcium chloride is more efficient than magnesium chloride upon both a weight basis and a molecular equivalent basis.

Commercial calcium chloride is obtained for the most part as a by-product in the manufacture of soda according to the ammonia or Solvay process. In this process concentrated sodium chloride brine is first saturated with ammonia gas (NH₃) and the ammoniacal brine thus made treated with carbon dioxide

(CO₂). The resulting reaction which produces ammonium chloride and bicarbonate of soda may be expressed as follows:

$$NaCl + H_2O + NH_3 + CO_2 = NH_4Cl + NaHCO_3$$
.

The sodium bicarbonate which is precipitated in this mixture is separated by suitable means and the mother liquor, containing ammonium chloride, some undecomposed sodium chloride and ammonium carbonate, is treated for the recovery of the ammonia present, by distillation with milk of lime. The reaction which produces calcium chloride is as follows:

$$2 \text{ NH}_4 \text{Cl} + \text{Ca}(\text{OH})_2 = 2 \text{ NH}_3 + \text{Ca}(\text{Cl}_2 + 2 \text{ H}_2\text{O}).$$

Ammonia thus passes off as a gas to be used over again and calcium chloride is left in solution together with a small amount of magnesium chloride and any undecomposed sodium chloride which may have passed through the operation. If the process of manufacture is conducted so as to transform all of the sodium chloride to carbonate, a solution of almost pure calcium chloride will be obtained as a by-product and this solution may be concentrated to any desired strength, or most of the water may be removed by evaporation and the calcium chloride obtained in solid form.

Calcium chloride can be purchased at a moderate price in an almost pure state. It is sold either in solution or in a solid, fused or granular condition. The solid material contains about 25 per cent moisture and 75 per cent calcium chloride. This represents about two molecules of H_2O per molecule of $CaCl_2$. In liquid form it may be purchased at any required dilution. The ordinary concentrated solution carries about 40 per cent calcium chloride and has a specific gravity of 1.402. Both the solid and solutions are sold on a basis of the actual calcium chloride content, and the solid is, therefore, cheaper when the cost of transportation is taken into account. It can at the present time be purchased in this country at from \$13.00 to \$16.00 per ton f.o.b., at points of manufacture. In England the same material may be had for about half this price, being sold for

30 s. (\$7.25) per ton. Because of this fact, and also on account of the generally moist climatic conditions encountered in England, it has been more extensively employed there than in this country.

It has, however, been used to some extent in the United States, and, when properly applied, has proved successful. The amount of salt and number of applications required to keep down the dust satisfactorily for a season will vary greatly with local conditions, but the exercise of a little judgment makes it possible to obtain good results with a minimum expense. Before considering its advantages and disadvantages, however, its method of application should be taken up.

Application of Calcium Chloride.—In most cases, calcium chloride is applied for the first time on the unprepared road, although when the road is extremely dusty it is desirable to have it first swept. The solution is sprinkled from an ordinary watering cart, so that on an average 0.4 gallon is applied per square yard, although by regulating the spread of the sprinkler to about two-thirds the width of the road, the middle receives twice the amount of the sides when the sprinkler passes over the road twice. While the center receives a double application by this means, there is a tendency for the salt to become uniformly distributed over the whole surface, owing to the fact that rains tend to carry it to the sides of the road. A 15 or 20 per cent solution is first employed and at least two of these applications made in the first week or two, in order to impregnate the surface thoroughly with the salt.

The salt thus applied has a tendency to retain moisture for a considerable length of time after an ordinary application of water would have evaporated. On hot dry days, however, the road does dry out, especially on portions unprotected by shade, and it has been found necessary to feed the salt by ordinary applications of water. The number of required sprinklings will, however, be greatly reduced. It is, of course, cheaper to feed the calcium chloride already on the road with water, than to apply a fresh solution each time the road becomes dry. In

humid weather it is often unnecessary to apply water for days at a time, as the salt absorbs sufficient moisture from the damp night air to keep the road in good condition throughout the succeeding day.

In the course of time, much of the calcium chloride is washed out of the road and has to be replaced by fresh material. Single sprinklings of an 8 or 10 per cent solution, applied at intervals varying from two to five weeks apart, according to conditions, are usually sufficient to maintain the proper amount, and these may be made in the same manner as described for the first two. A too rapid drying of the road is an indication that more salt is needed, and a little experience will soon enable the overseer or experimenter to determine just how often and at just what time to make a fresh application. The same is also true with respect to feeding the salt with water.

In regard to ascertaining and regulating the strength of the solution, the most convenient method is to determine its specific gravity by means of a hydrometer. Accurate determinations have been made of the specific gravity of solutions of known percentage composition, and, as hydrometers graduated to direct specific gravity readings can be obtained, the method is a very simple one. A hydrometer graduated from 1 to 1.4 is most suitable for ordinary work, and by comparing the readings with the following table, the strength of solution at 15° C. can be immediately ascertained. Also by diluting the salt or a concentrated solution with water, any desired strength may be obtained if the dilution is stopped at the specific gravity indicated for that particular strength.

A method has lately been devised and patented * for diluting and distributing materials miscible with water, which has many advantages as a time and labor saver. As this method is par-

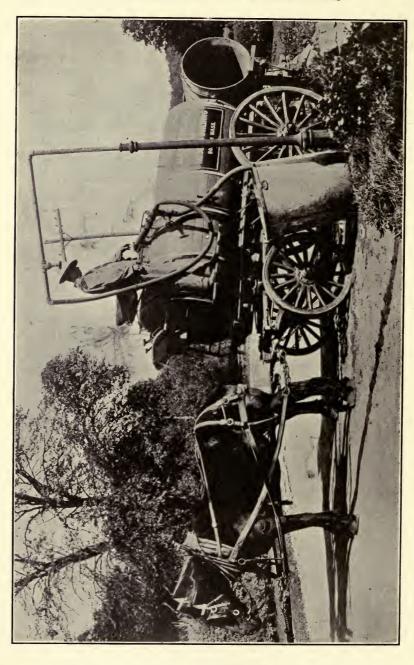
^{*} U. S. Patent No. 862,939, Aug. 13, 1907.

ticularly applicable to salt solutions, it may be well to describe it at this point. A watering cart is used similar to the ordinary type, with the exception of a rack attached to the rear. which is capable of holding a nest of five or six galvanized iron cans, each having a capacity of over 100 gallons. The wagon holds about 600 gallons. The cart is first loaded with the concentrated material, which is to be diluted. It is then driven to the first hydrant along the road. Here, a sufficient quantity of the material necessary to give the desired strength when diluted to the capacity of the wagon is drawn off into one of the cans. The wagon then proceeds to the next hydrant, where another lot is likewise unloaded, and so on. If the wagon has previously been loaded with a quantity equal to some multiple of the charges drawn off, a point will at last be reached where a quantity equal to that held by the separate cans remains in the wagon. Enough water is then run in from a hydrant to fill the wagon and the solution thus produced is applied to the road. Upon returning, the empty wagon is refilled at each of the hydrants beside which a can of the material has been left, the empty cans being returned to the rack. A siphon arrangement, as shown in Fig. 3, controlled by the water flowing from the hydrant, serves to lift the preparation into the wagon together with the water, thus producing the desired mixture. By employing a method of this sort, many unnecessary trips of the wagon are avoided and the cost of handling is reduced to a minimum.

Where a considerable amount of work is to be done with calcium chloride, the concentrated solution may be prepared or stored in large metal tanks set at an elevation sufficient to allow it to be run into the watering cart by gravity. Some time is required to dissolve the solid material, and, if it is not possible to secure a reservoir, the material should either be dissolved in the watering cart over night or else in the cans, which should have been previously distributed at the different hydrants.

When in the form of concentrated solutions it should not be stored in wooden casks or tanks, as its affinity for water is so





great that the moisture from the staves will be withdrawn and the shrinkage thus produced is apt to cause leakage.

While granulated calcium chloride dissolves quite readily in water, the fused product requires more time. Mechanical agitation will materially assist solution and should be employed when it is desired to dissolve the salt quickly. In cases where a solution is made over night, however, a good plan is to suspend the material in a wire net basket near the surface of the water. By this means a circulation of the liquid is produced, as the water in contact with the salt soon becomes a concentrated solution, which being heavier than the surrounding water sinks to the bottom of the vessel and thus allows fresh water to constantly attack it. If on the other hand the salt is placed in the bottom of the vessel, it is soon surrounded by a saturated layer of water which diffuses slowly and greatly retards further solution.

The principal advantages of calcium chloride as a dust layer are that it is odorless and clean. When present in sufficient quantity, it is undoubtedly a good dust layer if the atmosphere is somewhat humid, or if it is fed occasionally with water in dry weather. While it is true that the formation of mud in wet weather is not lessened, this mud is no more objectionable than that ordinarily encountered, as not enough salt is present to give it the undesirable qualities produced by the application of sea water. In addition, calcium chloride tends to distribute the moisture evenly over the road surface and it can be easily and quickly applied. Its use, like that of any other good dust layer, prolongs the life of a road by retaining the products of wear, and, in some cases, it may by chemical action increase the cementing value of the rock powder.

It has not to the author's knowledge been employed to any extent in the treatment of city streets. It would, however, seem to be well adapted for use as a dust layer for brick and block pavements which contain crevices where dust may accumulate in considerable quantities. Applied in solution to this type of pavement, it would soon find its way to the places where it was most needed and concentrating at these points

should remain efficient for a much longer time than when applied to a macadam road. It should also prove of considerable value for laying the dust on race tracks and on streets just before a parade. In some instances it has been employed in conjunction with various other materials to produce patented road preparations.

For macadam treatments its main disadvantage is that it is not essentially a road binder, and, at the end of a season's treatment, while the road may be in better condition than at the start, no additional wearing material will be present as, for instance, where a heavy bituminous binder has been used. Heavy rains are likely to wash most of it from the road, and if a number of showers follow soon after an application, much of its value will be lost. Water does not, however, always carry away as much of the salt as might be supposed, owing to the peculiar absorbent qualities of many rock powders.* Another objection to its use is that in hot dry weather it requires feeding with water sometimes as often as once a day. In common with all other temporary binders which are applied in solution or emulsion, it can only be employed in localities favored with a convenient water supply.

As a rule, it is slightly more expensive than water alone, but when applied intelligently according to a system similar to that described, the cost of treatment is in some measure reduced. In one case, under severe traffic conditions on a macadam road, the cost of laying the dust for one season was reduced from 3 cents per square yard with water alone to 2.7 cents with the use of calcium chloride. Six applications were made, two in June and one each in July, August, September and October, and, on very dry days, the road was given one light sprinkling with water. By this treatment, the dust was successfully laid throughout the season, while in previous seasons four applications of water a day often proved ineffective. Under certain conditions, therefore, calcium chloride may not only prove to be a good dust layer, but economical as well. And even if the cost is somewhat

^{*} See "The Effect of Water on Rock Powders," loc. cit.

greater than for the application of water alone, the beneficial effects produced upon the road will, in many cases, more than compensate this difference.

Examination of Calcium Chloride. — While, as has been stated, commercial calcium chloride or its solutions may be obtained in an almost pure condition, in some cases it contains noticeable quantities of impurities which lower its efficiency as a dust layer. When this is suspected, a determination should be made of the actual percentage of calcium chloride present. The principal impurities to be considered are calcium hydrate, magnesium hydrate, sodium chloride and magnesium chloride. When dealing with the solid salt the presence of calcium and magnesium hydrates, in any appreciable quantity, is indicated by failure of the salt to completely dissolve when treated with twice its weight of water. The concentrated 40 per cent solution, if clear, never contains a great amount of these substances, owing to their slight solubility in water.

CALCIUM.

The actual calcium chloride contents may be obtained in the following manner, which also necessitates a determination of sodium and magnesium chloride if present. Approximately I gram of the solid, or from 3 to 5 grams of the solution (depending upon its concentration) of the material to be examined is placed in a weighing bottle, which should be immediately stoppered and weighed. By subtracting the weight of the empty bottle, that of the material taken is ascertained. The contents of the bottle should next be dissolved or diluted with water. Any residue present should be filtered upon a 9 cm. filter paper and well washed with hot water, in order to separate it from the soluble material. The filtrate is then made up to 200 c.c. and divided into two aliquot portions, 1 and 2. Portion number I is evaporated on a steam bath to as near dryness as possible, taken up with a little hydrochloric acid, diluted with water and filtered as before. This filtrate is made up with water to 200 c.c. and again divided into two aliquot portions, a and b. Portion a is made decidedly ammoniacal and brought to a boil. A sufficient quantity of saturated solution of ammonium oxalate is then added to completely precipitate the lime and boiling continued for a few minutes. After settling, this precipitate is collected on a filter paper and washed with hot water, after which it is placed in a crucible, ignited, cooled in a desiccator and weighed. The weight of the crucible subtracted from this weight gives the weight of calcium oxide found. This weight multiplied by the factor 0.7148 gives the weight of calcium (Ca) present. In order to determine the percentage of calcium, it is, of course, necessary to multiply this figure by 4 and divide by the weight of material taken.

MAGNESIUM.

The filtrate from the calcium determination is made slightly acid with hydrochloric acid and an excess of concentrated solution of disodic phosphate added. It is then evaporated to a bulk not exceeding 150 c.c., transferred to an Erlenmeyer flask, and after cooling ammonia is added gradually with shaking until the reaction is strongly alkaline. The flask is stoppered with a smooth rubber stopper and shaken vigorously for five minutes. By this treatment the precipitate will usually be ready to filter inside of an hour. The filtrate should always, however, be preserved over night to make sure that no more precipitate appears. The precipitate is collected either on paper or a weighed Gooch crucible, burned, blasted and weighed as magnesium pyrophosphate (Mg₂P₂O₇) which multiplied by 0.2185 equals magnesium. The actual per cent of magnesium may be obtained as in the case of calcium.

SODIUM.

Portion b is neutralized with ammonium hydroxide, evaporated to dryness and heated below redness until the ammonium salts are driven off. The residue is then dissolved in a small amount of water, and milk of lime added in sufficient amount

to precipitate the magnesium if present. The mixture is then boiled for two or three minutes, filtered hot and washed thoroughly with boiling water. The lime in the filtrate is next precipitated with ammonia and ammonium oxalate and removed by filtration in the same manner as described under calcium, and the filtrate evaporated to dryness in a weighed platinum dish. The residue should be ignited below redness until all ammonium salts are driven off, cooled in a desiccator and weighed as sodium chloride. This weight multiplied by 0.3934 gives the weight of sodium found. The product so obtained, if multiplied by 4 and divided by the weight of material taken, gives the percentage of sodium.

CHLORINE.

Portion number 2 is made acid with nitric acid, brought to a boil, and the chlorine present precipitated as silver chloride with a solution of silver nitrate. The precipitate is then boiled for a few minutes and set away in the dark for a couple of hours, after which it is quickly filtered upon a weighed platinum Gooch crucible fitted with an asbestos pad, ignited to incipient fusion and weighed. This weight multiplied by 0.2474 gives the weight of chlorine present, and the per cent chlorine may then be obtained by multiplying this product by 2 and dividing by the weight of material taken.

CALCULATION OF RESULTS.

While the determinations as outlined above may be subject to some criticism from a strictly analytical standpoint, they are sufficiently accurate for all practical purposes, and will give a fair estimate of the amount of calcium chloride present in the original material. This may be determined in the following manner, by first calculating the amount of chlorine necessary to form chlorides of the magnesium and sodium present, subtracting this from the total amount of chlorine found and calculating the remainder to calcium chloride.

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Per cent magnesium \times 2.916 = (1) % chlorine as MgCl<sub>2</sub>

Per cent sodium \times 1.542 = (2) % chlorine as NaCl

(1) + (2) = % chlorine as MgCl<sub>2</sub> and NaCl.

Total per cent chlorine found... %

- chlorine as MgCl<sub>2</sub> and NaCl.... %

= chlorine as CaCl<sub>2</sub> 76 CaCl
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Per cent chlorine as $CaCl_2 \times \text{1.565} = \%$ $CaCl_2$.

If the percentage of calcium found is in excess of that required to satisfy the chlorine, the presence of calcium hydrate is indicated. Where it is desired to report the percentage of various impurities, the preceding results can, of course, be made use of if multiplied by the proper factors. In this case the residue remaining from the first filtration should be ignited and weighed as CaO, or if desired a complete analysis may be made of it according to any of the well-known methods of inorganic quantitative separation and analysis.

Sodium Silicate. — Sodium silicate, commonly known as water glass and having the formula Na₂SiO₃, has been employed to a slight extent as a dust preventive and road binder. It is prepared on a large scale by melting together quartz sand and sodium carbonate in proper proportions and also by melting together sodium sulphate, quartz sand and powdered charcoal. Upon exposure to the air or to carbonic acid gas gelatinous silicic acid, which under certain conditions acts as an excellent binding material, is precipitated from its solutions. It is extensively employed as a binding agent in the manufacture of artificial stone.

Sodium silicate has not been employed as a road binder to any extent and little or no data are to be had in regard to its value for this purpose. It may be applied in solution in the same general manner as calcium chloride and with some classes of basic roadstone, such as limestone, it will tend to cement the fragments together. It is the basis of a patented preparation known as Fitzsimons Patent Dust-layer, and has been employed in conjunction with various materials in other patented preparations. As ordinarily applied in weak solutions it can be regarded only as a semipermanent binder, although it acts as a permanent

binder when employed in comparatively large quantities in the manufacture of artificial stone. In the former case it is not present in sufficient quantity to produce a strong bond and the thin cementing films which are formed are apt to be broken under the action of traffic, and when once broken may not readily recement.

Commercial water glass is not of definite composition, and cannot be obtained crystallized. It may, however, be obtained in solution or in the solid amorphous state. The former usually has a specific gravity of about 1.38 and may be purchased in bulk at from 70 to 90 cents per cwt. The solid sells at from \$40.00 to \$45.00 per ton.

From solutions of metallic salts sodium silicate precipitates insoluble colloidal silicates of the metals. As these silicates act as binding materials, it would seem as though such reactions might be made use of when treating road surfaces. Thus the application of sodium silicate to a road, followed by an application of a soluble aluminum or calcium salt, such as aluminum sulphate or calcium chloride, has been suggested. By so doing, aluminum or calcium silicate, as the case may be, is precipitated in place on the road stone. It is extremely doubtful if such treatment will ever be extensively employed as the cost is apt to be high and the bond produced by no means permanent.

Other Salts. — A number of other inorganic salts have also been employed as dust layers and road binders, most of them being covered by patent. Among such may be mentioned a patented dust laying preparation known as Lyminite which is composed of sodium nitrate, sodium chloride, and lime. Potassium silicate has been suggested as a road binder, its action being similar in every respect to sodium silicate. It is, however, in common with all potassium compounds, much more expensive than the corresponding sodium products and therefore not as likely to be used for road treatment. Certain compounds of a mineral base with an organic acid have been employed to some extent, but these materials will be considered in the following chapter on non-bituminous organic materials.

Rock Dust. — Many rock powders under favorable conditions are capable of developing considerable binding or cementing value. Mention of this fact has already been made when discussing the action of various dust layers, particularly water, upon broken stone roads. Certain rock powders may be considered as semipermanent and in some cases even as permanent road binders. For the most authoritative and valuable information on this subject reference should be made to a number of papers by Page and Cushman.* These are here quoted at some length as the facts demonstrated therein have a most important bearing upon the subject of dust prevention and road preservation, and, as will be shown later, the cementing value of the rock dust produced on a road will often influence the selection of an auxiliary binder if such is needed.

In regard to the causes of the cementing power of rock powders these investigators concluded that they must be closely associated with those which produce the same property in clays. To quote † - "The whole question of the binding power of rock dust was early recognized as being clearly associated with the same property in clays. In fact considered from the standpoint of road materials, it is difficult to determine where the classification as clay should stop; that is to say, clays pass imperceptibly into gravels. Some gravels which contain a proportion of clay base will be found to bind, while a clean quartz gravel absolutely lacks this property. While this is easily understood, it does not, on first examination, seem to have any bearing upon the great difference in binding power which is exhibited by clean, deep quarried rock. It will be found, however, that the considerations are identical. Clays themselves are the product of rock decay under the action of water and watery solutions. The essential clay base is supposed to be a hydrated silicate of aluminum, known as kaolin, which is the result of the action of water on the double silicates of aluminum and the alkali metals. The most typical of the double silicates are the feldspars, a class of

^{*} Loc. cit., p. 40.

[†] Bulletin No. 85, Bureau of Chemistry, U. S. Dept. of Agriculture.

minerals very widely distributed in nature and occurring as a crystalline ingredient of a great number of different rock species. The microscopical analysis of rocks shows that a great many of the minerals which make up the aggregate structure have undergone secondary changes similar to, if not identical with, kaolinization of feldspar. Now kaolin, as found in nature, although not lacking in binding power, does not, as a rule, excel in this quality. The ball clays are usually added by potters to the purer kaolins and china clays to increase both the plasticity and the binding power. It is very evident that binding power is not due to the presence of a particular mineral such as kaolinite; on the contrary, the higher binding clays show a preponderance of amorphous rather than of crystalline particles.

"The evidence obtained points to the following conclusions: Many minerals under the action of water or of watery solutions are decomposed. The secondary products, which are usually highly hydrated, may or may not lead to binding power, as they. are capable of existing in allotropic modifications which differ in this respect. Alumina and many other substances can be easily prepared by wet reactions in the laboratory, either as gummy colloids or as finely crystalline precipitates, by slightly varying the conditions. In nature the conditions are of every possible variety, and thus we find a physical property like cementing power varying through wide limits in those rock species which exhibit it. In a word, those rock dusts which contain a certain proportion of particles which on soaking with water soften to the extent that they become, to ever so slight a degree, glue-like (colloid), and thus adhere, are those which are useful to the road builder. Many of the traps, limestones and sandstones, fall under this head. Those rocks, on the other hand, which are of an entirely unaltered crystalline structure, or those which, through metamorphic changes — heat and pressure — have had the active hydrated particles destroyed—such as slates and quartzites - should be avoided on the surface portion of the road.

"These conclusions are borne out in service where the problem has to be solved of building roads of material which, while hard enough to bear traffic, is without binding power. A good example is furnished by the excellent sand-clay roads in the southern states. A somewhat similar case is that of burnt-clay roads. Clay itself, as every one knows, is generally too soft and plastic to bear traffic in wet weather, although its binding power is high. By burning and clinkering a portion of the clay to be used on the road its hardness is increased and its binding power destroyed. By proper constructive methods and mixing we approach the conditions obtained with rock dust and with sand clay mixtures."

In another paper by Cushman* on "The Effect of Water on Rock Powders," the following conclusions are reached: (1) "When water comes in contact with most rock powders, immediate reactions take place, which are to a certain extent analogous to those which take place with cement and powdered glass." (2) "The microscope reveals an accumulation of amorphous material of a gummy appearance largely associated with the surfaces of the crystalline particles as the action of water proceeds." (3) "The effect of wet grinding is to increase the binding power or the cementing value of rock powders, and there are indications that the addition of small amounts of suitable electrolytes" (soluble inorganic salts, acids, and bases) "to the water will still further increase the action."

The last fact has a decided bearing upon the road binding value of the inorganic dust layers and road binders already described and also upon the effect of blending different roadstones, one of which through being partially soluble is capable of reacting upon the other to produce binding films. It has been noticed in cases in which macadam roads were being constructed of hard material, such as granite or diabase, which are difficult to bond under the roller, that the surface quickly compacted and gave satisfactory results when treated with a top dressing of limestone screenings. This observation led Cush-

^{*} Bulletin No. 92, Bureau of Chemistry, U. S. Dept. of Agriculture.

man and Hubbard* to determine the cementing value of mixtures of these rocks with limestone as compared with the cementing values of the individual rocks. For this purpose recourse was had to the cementation test as conducted in the laboratory of the United States Office of Public Roads, which will be described later. This work was conducted during an investigation of the "Decomposition of the Feldspars," granite being a type of feldspathic rock. The results of a number of tests are given below and show conclusively that the addition of limestone to a feldspathic rock increases the binding power.

RESULTS OF TESTS OF THE CEMENTING VALUE OF GRANITE MIXED WITH LIMESTONE.

| Granite. | Limestone. | Cementing Value. | | | | | | |
|------------|--------------|------------------|------------|----------------------|--|--|--|--|
| Granite. | Diffiestone. | Granite. | Limestone. | Mixture. | | | | |
| Serial No. | Serial No. | | | | | | | |
| 1431 | 1391 | 3 | 27 | 110 | | | | |
| 1432 | 1342 | 9 | 22 | 56 | | | | |
| 1435 | 1335 | 7 | 26 | 38 | | | | |
| 1435 | 1423 | 7 | 26 | 56 38 53 82 | | | | |
| 1574 | 1411 | 6 | 20 | 82 | | | | |

As the binding power of rock dusts is due to the decomposition or hydrolysis brought about by the action of water, it would follow that if this binding power can be increased by the addition of limestone it is caused by further decomposition of the material, brought about by the interaction of calcium hydroxide $(Ca(OH)_2)$, resulting from the hydrolysis of the limestone particles. This is demonstrated by the following results obtained by determining the cementing value of a number of granites when treated with a small quantity of limewater, or calcium hydroxide solution.

^{*} Bulletin No. 28, Office of Public Roads, U. S. Department of Agriculture.

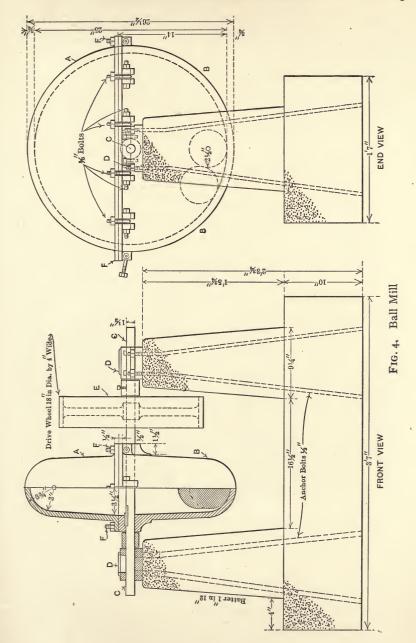
RESULTS OF TESTS OF THE CEMENTING VALUE OF GRANITE MIXED WITH LIMEWATER,

| | Cementin | g Value. | | Cementing Value. | | |
|--|---------------------------------------|--|--|-----------------------------------|----------------------------------|--|
| Serial No. | Alone. | Alone. With Limewater. | | Alone. | With Limewater. | |
| 810 811 817 893 1008 1192 | 12 6 11 12 35 14 16 | 21 16 21 16 45 27 39 | 1276 1329 1398 1431 1432 1435 1574 | 11 10 6 3 9 7 6 | 31 44 18 19 12 15 | |

These results show in every case a considerable increase in the cementing value of granites so treated and would indicate that the addition of a small amount of lime might greatly improve the binding value of certain roadstones. Of course the addition of a sufficient quantity of lime would produce a mortar in which the bond due to the crystallization of calcium carbonate will cover up any actual increase in the cementing value of the stone treated. This effect will also be produced to some extent when even a small quantity of lime is employed, but results given by Lord,* who applied the principles developed by Cushman for rock powders, show that when a sample of chert and one of clinker were so treated the increase in cementing value was greatly in excess of that produced by treating a chemically inert slag in a similar manner. These results are given below and indicate that the increase in cementing value is due to the formation of a hydrated silicate of lime.

| | | Cementing Value. | | | | | | | |
|-----------|--|------------------|---------------|-----------------|-----------------------|---------------------|--|--|--|
| Material. | Mineral Composition. | Alone. | With 1% CaO. | With 4% CaO. | With 8% CaO. | With 13% CaO. | | | |
| Chert | Olivene and gehlenite Amorphous quartz Acid silicate | 8 6 4 | 15 9 24 | 33 22 60 | 5 ² 106 | 95 2000+ 1400 | | | |

^{* &}quot;The Composition and Properties of Slag for Road Making." Paper read before the Seventh International Congress of Applied Chemistry, London, 1909.



The conclusions to be drawn from all of these tests are that mixtures of acid and basic rocks show a higher cementing value than either alone, and that it is possible by selecting and blending certain roadstones, or by treating the road with a suitable chemical salt or base, to greatly increase the natural bond of the road surface.

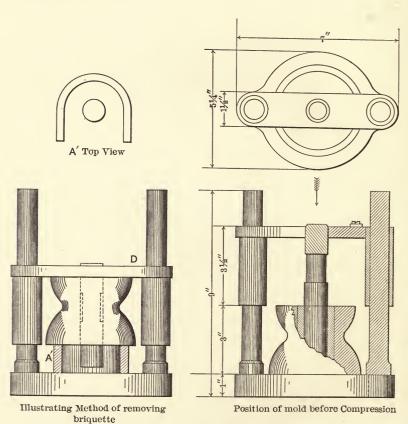
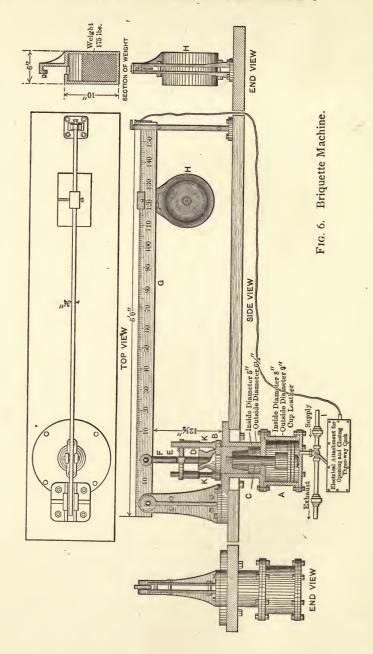


Fig. 5. Briquette Mold.

Determination of the Cementing Value of Rock Powders.— The cementation test for rock powders as conducted by the U. S. Office of Public Roads is made as follows. Five hundred grams of the coarsely crushed rock sample, broken to pass a one-half inch mesh, and 90 c.c. of water are placed, together with two steel shot r_3 cm. in diameter, in a ball mill. (See Fig. 4.) This is a circular cast iron mill, consisting of two unequal segments A and B which should be bolted together after the charge has been placed inside. It revolves in a vertical plane about the shaft CC, which bears in the pillow blocks DD, and is driven from the pulley E at the rate of 2000 revolutions per hour. The sample is ground for two and one-half hours, the action of the steel shot reducing the rock sample to a stiff dough, in which condition it is ready to be molded into briquettes. About 25 grams of this dough are placed in a cylindrical metal die 25 mm. in diameter, shown in Fig. 5. A closely fitting plug supported by guide rods is inserted over the material, which is then molded in the briquette machine, Fig. 6.

In this machine the hydraulic cylinder A supports an iron platform B through the piston rod C. The cylindrical metal die containing the material to be compressed is placed upon the platform and water admitted to the cylinder through the supply pipe I. As the piston rises, the platform and die are carried up with it, the plug of the latter coming in contact with a properly weighted lever arm G. The weight H is adjusted on the lever arm so as to give a maximum pressure of 132 kilos per sq. cm. on the compressed material, which pressure is applied only for an instant. The total time of compression up to the maximum is about 30 seconds. When the lever arm is raised one-eighth of an inch it closes an electric circuit which trips a right-angle cock, shutting off the water and opening the exhaust.

The briquette is removed from the die and its height measured. If it is not exactly 25 mm. the requisite amount of material is added or subtracted to make the next briquette the required height. Five briquettes are made from each test sample and allowed to dry 20 hours in air and 4 hours in a hot air bath at approximately 100° C. After cooling 20 minutes in a desiccator they are tested by impact in a machine especially designed for



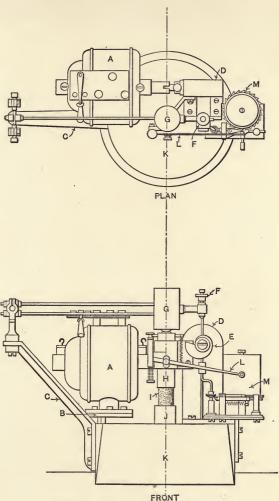


Fig. 7. Page Impact Machine.

the purpose and known as the Page Impact Machine. In this machine (Fig. 7) the motor A drives the cam E at the rate of 60 revolutions per minute, by means of a worm gear. The hammer G, weighing 1 kg., is raised by means of the adjustable pin F, which slides over the face of the cam. With the one-half kg. plunger H resting on the briquette I, the end of pin F is brought

in contact with the cam as indicated in the figure, and the binding nut is tightened to hold the pin in position. The bottom of the plunger is pressed upon the briquette by two spiral springs. The rise of the cam is such as to give an effective drop of one centimeter to the hammer. The reaction of the briquette after each blow of the hammer produces a vertical movement in the end of the lever L. This motion is recorded on a sheet of silicated paper wrapped around the recording drum M by means of a brass point at the end of lever L. Each revolution of the cam produces a slight motion of the drum so that the drum makes a complete revolution for 100 revolutions of the cam. The number of blows necessary to destroy the resilience of the briquette, so that no reaction is recorded on the drum, and the average obtained upon five briquettes is taken to be the cementing value of the material. As compared with the results of service, a cementing value of 10 is low, 20 is fair, 40 is good and all values above 50 are excellent.

Slaking Test of Rock Powder, Briquettes. - Different rock powders after briquetting often behave quite differently if allowed to stand under water. Work in the laboratory of the Office of Public Roads has shown that some will rapidly slake or disintegrate in the same manner that a lump of fat clay slakes under water, and that others slake very slowly or not at all. This property seems to be quite independent of the cementing value of the rock powder as ordinarily determined, and as it has a very direct bearing upon the way a stone binder will behave upon the road in rainy weather, should be determined before selecting a roadstone. The test is made by placing the briquette which has been molded and dried in the manner described under the cementation test, under water at 20° C. and noting the time required for it to slake. Other things being equal, preference should be given to rock powders which slake slowly or not at all over those which slake rapidly, for it is evident that a fast slaking rock powder, if employed as a road binder, will produce a muddy surface in wet weather.

Slag Powders. — In the manufacture of iron and steel, immense quantities of slag are produced in this country as by-products. Many of these slags are not unlike certain classes of rock in their physical characteristics, and they have been employed to some extent as road materials. In the paper by Lord, before referred to, the results of an investigation of the cementing value of slags are given, and these results would seem to be of great interest in connection with the selection and use of slag screenings or slag dust as a binder for macadam roads. As in the case of rock powders, it was found that the cementing value of slag is caused to a large extent by the hydration of certain minerals readily attacked by water, and that owing to variations in mineral composition, this property varies greatly in different types of slag. In general the cementing value of a slag is a function of its solubility in water, and this fact has been made the basis of a rapid test for determining whether a slag will act as a good or poor road binder. As a rule, those showing the highest cementing value were found to contain silicate minerals identical in crystal form and chemical composition with the active elements, alite and belite, of hydraulic cements. The bond produced in briquettes made from this type of slag is, therefore, similar to that produced in cement and, as shown in the following tables, the cementing values run high. minerals mentioned are readily attacked by water, and those slags containing a relatively large proportion of lime in solid solution, therefore, exhibit the highest cementing values. The relative solubility of a slag is indicated in a rough way by Cushman's method * of treating a portion of the finely ground powder to which water has been added with a few drops of a r per cent alcoholic solution of phenolphthalein. When thus treated, the more soluble slags produce a dark red solution, the slightly soluble a faint pink and the practically insoluble slags a colorless solution. The relation between this test and the cementing value of the slag powder as determined by Lord is shown in the table below.

^{* &}quot;The Effect of Water on Rock Powders," loc. cit.

| COLORIMETRIC TESTS (| OF SLAG POWDERS WITH | | | | | | | |
|----------------------|----------------------|--|--|--|--|--|--|--|
| PHENOLPHTHALEIN. | | | | | | | | |

| (| Basic Slags. | |] | Intermediate Sla | gs. | Acid Slags. | | | |
|----------------------------------|---|------------------------------|--------------------------------|---|-----------------------------------|----------------------------|---|-------------------------------|--|
| No. | Color. | Cementing Value. | No. | Color. | Cementing Value. | No. | Color. | Cementing Value. | |
| 23 25 26 27 28 29 | Colorless Colorless Deep red Deep red Deep red Deep red | 17 8 109 596 463 | 8 9 12 13 14 15 | Faint pink Deep pink Faint pink Deep pink Colorless Deep pink | 31 24 20 156 15 62 | 1 2 3 4 6 7 | Colorless Colorless Colorless Colorless Colorless Colorless | 5 10 3 3 16 11 | |

As will be noticed, this investigator classifies slags under three heads, basic, intermediate and acid, and this classification is made according to their silica contents, the basic slags being comparatively low and the acid comparatively high in silica. Intermediate types are by far the most common and generally have a semicrystalline texture and are light gray in color. To this class belong most of the blast furnace slags. The cementing value of these slags may usually be greatly increased by the addition of small amounts of lime. As an example of this fact. Lord cites the case of a blast furnace slag having an original cementing value of 15 which was increased to 200, 426, and 2000 by the addition of 1, 4 and 8 per cent of CaO respectively. Slags, obtained from the open hearth furnaces, carrying an excess of lime give invariably a deep color with phenolphthalein and have as has been shown excellent cementing values. They would, therefore, appear to be especially adapted for use as road binders. Experimental sections of road built under the direction of the U.S. Office of Public Roads at Youngstown, Ohio, during the summer of 1909, in which open hearth slag screenings and blast furnace slag screenings mixed with 5 per cent lime were employed, have so far shown these materials to be very good road binders as compared with stone screenings.

It is very doubtful, however, if slag will ever prove to be an entirely satisfactory binder for roads subjected to a great amount of mixed traffic, because of the rigid nature of the bond produced, and the fact that if the bond is once broken it will not form again except in the presence of water. Such material may of course prove serviceable on roads subjected to light traffic and has the advantage of being inexpensive in localities near which it is produced. Best results will probably be obtained where the climate is rather rainy than otherwise, as the slag develops its greatest binding value when subjected to the action of water for extended periods. Under these conditions the open hearth slag powders in particular, if of proper mineral composition, show all the properties of a slow setting hydraulic cement.

The use of slag screenings is limited to broken stone roads and when employed on such roads they should be applied in exactly the same manner as stone screenings in macadam road construction. They should be as fine as possible and after being spread upon the upper course of stone should be thoroughly puddled with water and well rolled. After the road is finished it is good practice to close it, if possible, to traffic for at least a week and during that time to sprinkle it daily with a copious supply of water. By so doing the slag can develop a good set which will better withstand the grind of traffic than the initial bond produced. The use of calcium chloride solutions upon slag bonded roads would also seem to be advisable, as by this means moisture is retained in contact with the slag particles for considerable periods and a stronger bond is thus produced than if water alone is applied.

CHAPTER IV.

INORGANIC DUST PREVENTIVES AND ROAD BINDERS.—Continued.

Hydraulic Cements in General. — Hydraulic cements are undoubtedly the most powerful of all known road binders and in all probability will play an important part in the road of the future. As permanent binders in foundation courses they cannot be excelled, but for road surfaces they are open to some criticism. The use of hydraulic cements in road work has been so exhaustively treated in a number of textbooks on road and pavement construction, that it seems hardly necessary in this book to discuss the subject in all of its details. As the subject of road binders would, however, be incomplete without at least a brief description of their characteristics and the methods of employing them, it has seemed well to the author to devote some space to their consideration.

Hydraulic cements are so called because of their property of hardening or setting under water. They may be conveniently divided into three groups, natural, Portland and puzzolan. The setting property of all of these cements is due to reactions which take place when they are brought in contact with water. While these reactions are complex and not well understood at the present time, they are known to be due to the presence of certain minerals which readily break down under the action of water and produce other compounds of both a colloidal and crystalline nature, which interlock and produce a set. Two of these minerals, alite and belite, which are found in Portland cement have already been mentioned as occurring in certain kinds of slag. While the mineral composition of a cement is of course dependent upon the relative proportion of the chemical elements present, and while these proportions are neces-

sarily confined within rather narrow limits, the fact that under varying conditions of manufacture the elements may combine in a number of different ways to form different classes of minerals makes a chemical analysis of a cement of little value in determining its physical properties. Recourse is, therefore, had to physical tests for the purpose of determining the value of a cement for the work for which it is intended. These tests will be taken up after briefly considering the individual types and the use of such materials in general as road binders.

For the purpose of ascertaining the hydraulic possibilities of a cement, use is made of a formula for determining what is known as the Cementation Index. For all practical purposes the active compounds contained in these cements may be considered as tricalcic silicate (3 CaO . SiO₂) and dicalcic aluminate (2 CaO. SiO₂), although the subject of constitution is still an open question and will not here be discussed. It is customary to consider magnesia (MgO) as molecularly interchangeable with lime (CaO), and iron oxide (Fe₂O₃) with alumina (Al₂O₂). The cementation index is the ratio of silica, alumina and iron oxide to lime and magnesia as expressed with reference to their combining values for the two compounds mentioned. In order that it may be employed, it is of course necessary to know the percentages of the oxides of the various elements present, and this can only be determined by chemical analysis. The formula for the cementation index may be expressed as follows:

Cementation Index =

$$\frac{(2.8\times\%~\mathrm{SiO_2}) + (1.1\times\%~\mathrm{Al_2O_3}) + (~\mathrm{o.7}\times\%~\mathrm{Fe_2O_3})}{\%~\mathrm{CaO}~+ (1.4\times\%~\mathrm{MgO})}.$$

Except within certain limits the chemical analysis and, therefore, the cementation index are of little value in determining the physical properties of a cement, unless the cement has been well burned. It is, however, of considerable value as a means of classification, as will appear later. Any cement with an index lower than I must contain free lime, no matter at how high a

temperature it has been burned, and free lime is known to injuriously affect its soundness.

Natural Cements. — Natural cements are produced by burning natural argillaceous limestones, containing from 15 to 40 per cent silica, alumina and iron oxides, in a kiln without previous mixing and grinding. The temperature of burning is about the same as that of an ordinary limekiln. The resulting product is then ground fine, after which it exhibits hydraulic properties.

Natural cements are generally yellow to brown in color and run from 2.7 to 3.1 specific gravity. The cementation index of most American natural cements lies between 1.15 and 1.60. If this index runs lower than 1.15 the cement may be considered as a natural Portland and if burned at a sufficiently high temperature will exhibit much the same properties as a good Portland cement; otherwise it is apt to contain a large amount of free lime, which is considered detrimental. Natural cements of this type should have a high specific gravity, that is, over 3.0. As the cementation index increases above 1.60 the hydraulic properties of the cement decrease.

According to standard specifications adopted by the American Society for Testing Materials in 1904, and amended in 1909, natural cements should show the following properties.

NATURAL CEMENT.

Definition. — This term shall be applied to the finely pulverized product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

SPECIFIC GRAVITY.

The specific gravity of the cement thoroughly dried at 100° C. shall be not less than 2.8.

FINENESS.

It shall leave by weight a residue of not more than 10 per cent on the No. 100, and 30 per cent on the No. 200 sieve.

TIME OF SETTING.

It shall develop initial set in not less than ten minutes, and hard set in not less than thirty minutes, nor more than three hours.

TENSILE STRENGTH.

The minimum requirements for tensile strength for briquettes one inch square in cross section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

| Age | э. | Neat Cement. | Strength. |
|-----|----------------|---|-----------|
| 24 | hours in moist | air | 75 lbs. |
| 7 | days (1 day in | moist air, 6 days in water) | 150 lbs. |
| 28 | days (1 day in | moist air, 27 days in water) | 250 lbs. |
| | One Pa | art Cement, Three Parts Standard Ottawa Sand. | |
| 7 | days (1 day in | moist air, 6 days in water) | 50 lbs. |
| 28 | days (1 day in | moist air, 27 days in water) | 125 lbs. |

CONSTANCY OF VOLUME.

Pats of neat cement about three inches in diameter, one-half inch thick at center, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

- (a) A pat is then kept in air at normal temperature.
- (b) Another is kept in water maintained as near 70° F. as practicable.

These pats are observed at intervals for at least twenty-eight days, and, to satisfactorily pass the tests, should remain firm and hard and show no signs of distortion, checking, cracking or disintegration.

Portland Cements. — Portland cements are produced by burning to incipient fusion an intimate artificial mixture of finely ground calcareous and argillaceous materials, consisting of approximately three parts of calcium carbonate (CaCO₃) to one part of silica, alumina and iron oxide, and afterwards finely pulverizing the clinker. This fusion is usually produced in a rotary kiln and at a much higher temperature than that employed in the manufacture of natural cements. Portland cement is commonly blue to gray in color and runs from 3 to 3.2 specific

gravity. Its cementation index should be between 1.0 and 1.2, preferably nearer the first figure than the latter. In general Portland cements will show from 59 to 67 per cent CaO, from 19 to 24 per cent SiO_2 and from 9 to 13 per cent $Al_2O_3 + Fe_2O_3$. Magnesia to the extent of over 4 per cent is regarded as injurious.

According to standard specifications adopted by the American Society for Testing Materials in 1904, and amended in 1909, Portland cements should show the following properties.

PORTLAND CEMENTS.

Definition. — This term is applied to the finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, and to which no addition greater than 3 per cent has been made subsequent to calcination.

SPECIFIC GRAVITY.

The specific gravity of the cement, thoroughly dried at 100° C., shall be not less than 3.10. Should the test of cement as received fall below this requirement, a second test may be made upon a sample ignited at a low red heat. The loss in weight of the ignited cement shall not exceed 4 per cent.

FINENESS.

It shall leave by weight a residue of not more than 8 per cent on the No. 100, and not more than 25 per cent on the No. 200 sieve.

TIME OF SETTING.

It shall develop initial set in not less than thirty minutes, but must develop hard set in not less than one hour, nor more than ten hours.

TENSILE STRENGTH.

The minimum requirements for tensile strength for briquettes one inch square in section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

| Age. | Neat Cement. | Strength. |
|------|--|-----------|
| 24 | hours in moist air | 175 lbs. |
| 7 | days (1 day in moist air, 6 days in water) | 500 lbs. |
| 28 | days (1 day in moist air, 27 days in water) | 600 lbs. |
| | One Part Cement, Three Parts Standard Ottawa Sand. | |
| 7 | days (1 day in moist air, 6 days in water) | 200 lbs. |
| 28 | days (1 day in moist air, 27 days in water) | 275 lbs. |

CONSTANCY OF VOLUME.

Pats of neat cement about three inches in diameter, onehalf inch thick at the center, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

- (a) A pat is then kept in air at normal temperature and observed at intervals for at least twenty-eight days.
- (b) Another pat is kept in water maintained as near 70° F as practicable, and observed at intervals for at least twenty-eight days.
- (c) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel for five hours.

These pats, to satisfactorily pass the requirements, shall remain firm and hard and show no signs of distortion, checking, cracking or disintegrating.

SULPHURIC ACID AND MAGNESIA.

The cement shall not contain more than 1.75 per cent of anhydrous sulphuric acid (SO₃), nor more than 4 per cent of magnesia (MgO).

Puzzolan Cements. — (Slag cement.) The only type of puzzolan cement which will be considered is slag cement, which is coming to be extensively used in this country. According to Eckel,* "Slag cement is composed of an intimate mechanical mixture of slaked lime and granulated blast furnace slag of suitable chemical composition, both materials being finely pulverized before, during or after mixing. The process of manufacture

^{* &}quot;Cements, Limes and Plasters," p. 641, Wiley and Sons.

includes the granulating and drying of the slag, the slaking of the lime, the mixing of the materials, and the grinding of the resulting cement, together with every means which may be employed for the regulation of the setting of the cement." Ordinarily slag cements set very slowly as compared with Portland cements and small quantities of caustic soda, potash, sodium chloride or similar salts are added to reduce the time of setting. The color of these cements as a class varies from light blue to lilac and their specific gravity from 2.7 to 2.9. From the analysis of several American slag cements, Eckel has calculated their cementation index as being 1.59 or over. This is far above the cementation index of Portland cement, and is due to the fact that they contain a much lower percentage of lime and magnesia than the Portlands.

Specifications regarding gravity, fineness, time of setting, tensile strength and soundness which have been employed in this country are as follows. These specifications constitute a part of the "Specifications for Puzzolan Cement," published in 1902 by The Engineer Corps, U. S. Army, and are given for the sake of comparison with those for Natural and Portland Cement, adopted by the American Society for Testing Materials.

PUZZOLAN CEMENT.

SPECIFIC GRAVITY.

The specific gravity of the cement, as determined from a sample which has been carefully dried, shall be between 2.7 and 2.8.

FINENESS.

Ninety-seven per cent must pass through a sieve made of No. 40 wire, Stubb's gauge, having 10,000 openings per square inch.

TIME OF SETTING.

The cement shall not acquire its initial set in less than forty-five minutes and shall acquire its final set in ten hours. . . .

TENSILE STRENGTH.

Briquettes made of neat cement, after being kept in air under a wet cloth for twenty-four hours and the balance of the time in water, shall develop tensile strength per square inch as follows:

After seven days, 350 pounds; after twenty-eight days, 500 pounds.

Briquettes made of one part cement and three parts standard sand by weight shall develop tensile strengths per square inch as follows:

After seven days, 140 pounds; after twenty-eight days, 220 pounds. . . .

SOUNDNESS.

To test the soundness of cement, pats of neat cement mixed for five minutes with 18 per cent of water by weight shall be made on glass, each pat about three inches in diameter and one-half inch thick at the center, tapering thence to a thin edge. The pats are to be kept under wet cloths until finally set, when they are to be placed in fresh water. They should not show distortion or cracks at the end of twenty-eight days.

Use of Cements. — Mixtures of hydraulic cement, sand, gravel or broken stone and water have been so extensively employed in the construction of cement concrete foundations for roads and pavements and their use for this purpose is so well understood by road engineers, that this phase of the subject requires but passing mention. The correct proportions of the various constituents of such concretes will of course vary with the character and size of the local material which will be employed as the mineral aggregate. A good foundation should be homogeneous, compact, waterproof and of sufficient strength to carry without rupture the heaviest load to which the road is to be subjected, and this can best be obtained by the use of a good cement so proportioned and mixed with the mineral aggregate that voids are reduced to a minimum. (For a method of obtaining dense aggregates see page 303.) These points are dis-

cussed in detail in nearly all books having to do with the construction of roads and pavements. The concrete may be mixed either by hand or machinery, preferably the latter on account of greater uniformity in the resulting product. A modern portable cement concrete mixing plant is shown in Fig. 8. The proportions of the ingredients required should be determined by measuring the percentage of voids in each material and water should be added in quantity just sufficient to produce a coherent plastic mass.

According to Byrne,* "The following are some of the more usual proportions:"

| American hydraulic cement | ı part |
|---------------------------|-----------------------|
| Sand | 2 parts. |
| Broken stone | 3 parts |
| Portland cement | ı part. |
| Sand | 3 parts. |
| Broken stone | 5 to 7 parts. |
| Portland cement | ı part. |
| Sand | $2\frac{1}{2}$ parts. |
| Gravel | 3 parts. |
| Broken stone | 5 parts. |

The mixed cements should be laid and rammed in layers not exceeding 6 inches in thickness, until water begins to ooze out on the upper surface. It should then be allowed to set for at least twelve hours without being disturbed in any way.

While cement is admittedly a most superior binding medium for foundations and should be so employed when circumstances permit, its value as a binder in the wearing surface of a road is of more interest in connection with the subject of this book. Undoubtedly the most enduring type of cement wearing surface is cement concrete mixed and laid in much the same manner as described for cement concrete foundations. For such wearing surfaces Portland cement is usually to be preferred to the other types. The latter may, however, be employed to advantage in foundation work. Owing to their rigidity cement wearing sur-

^{* &}quot;Highway Construction," 5th Ed., p. 387, Wiley and Sons.



Fig. 8. Modern Portable Cement Concrete Mixing Plant.

faces should be laid only on foundations of like rigidity, and this necessitates the construction of an entire cement concrete pavement, which at the present time is entirely too costly for ordinary country roads.

One of the cheapest forms of concrete road, from the stand-point of construction, is known as the Hassam Pavement, which is covered by patent.* In the construction of this road graded broken stone of suitable dimensions is laid and compacted to the required depth, which is about that of an ordinary macadam, and is then flushed with a thin grout of sand and Portland cement, in the proportion of 2 to 1. By this means it is expected that the voids in the stone aggregate will be filled to a great extent, and to aid in forcing the grout into the road, rolling and tamping are resorted to until a thin layer of grout remains permanently upon the surface. A light course of pea gravel is then spread over the surface and well rolled.

Cement concrete roads may also be built by dry mixing graded stone, sand and cement in proper proportion. The dry mixture is spread upon the road and consolidated in the same manner as an ordinary macadam with the use of water. Such roads are, however, apt to be non-homogeneous, owing to the fact that the cement, being the finest ingredient, tends to concentrate at the bottom of the road, thus leaving the surface poor in binding material.

A good cement wearing surface has the advantage of being practically waterproof, smooth to any desired extent according to the method of finishing, easily cleaned and non-absorbent of heat. It is well fitted for automobile traffic alone, but the pound of horses' hoofs and the grind of heavily loaded steel tired wheels cause considerable wear which is productive of dust. It is a noisy form of pavement, possesses but little resiliency and is, therefore, hard on horses. If treated with a thin coat of heavy bitumen, as will be described later, its undesirable properties are somewhat modified. Everything considered, hydraulic cements compare quite favorably with other kinds of road binders and by some are thought to approach the ideal more

^{*} U. S. Patent No. 851,625, April 23, 1907.

closely than any other. The general trend of experimental work, however, seems to favor the use of a bituminous binder.

Cement Testing. — Perhaps no better methods of cement testing can be given than those included in the progress report of a committee appointed by the American Society of Civil Engineers to examine methods of making cement tests. This report, as made in 1903 and amended in 1904, is presented below:

- SAMPLING. Specimens Representa

- I. Selection of Sample. The selection of the sample for testing is a detail that must be left to the discretion of the engineer; the number and the quantity to be taken from each package will depend largely on the importance of the work, the number of tests to be made and the facilities for making them.
- 2. The sample shall be a fair average of the contents of the package; it is recommended that, where conditions permit, one barrel in every ten be sampled.
- 3. All samples should be passed through a sieve having twenty meshes per linear inch, in order to break up lumps and remove foreign material; this is also a very effective method for mixing them together in order to obtain an average. For determining the characteristics of a shipment of cement, the individual samples may be mixed and the average tested; where time will permit, however, it is recommended that they be tested separately.
- 4. Method of Sampling.—Cement in barrels should be sampled through a hole made in the center of one of the staves, midway between the heads, or in the head, by means of an auger or a sampling iron similar to that used by sugar inspectors. If in bags, it should be taken from surface to center.

CHEMICAL ANALYSIS.

5. Significance. — Chemical analysis may render valuable service in the detection of adulteration of cement with considerable amounts of inert material, such as slag or ground limestone. It is of use, also, in determining whether certain

constituents, believed to be harmful when in excess of a certain percentage, as magnesia and sulphuric anhydride, are present in inadmissible proportions. While not recommending a definite limit for these impurities, the committee would suggest that the most recent and reliable evidence appears to indicate that, for Portland cement, magnesia to the amount of 5 per cent, and sulphuric anhydride to the amount of 1.75 per cent, may safely be considered harmless.

- 6. The determination of the principal constituents of cement silica, alumina, iron oxide and lime is not conclusive as an indication of quality. Faulty character of cement results more frequently from imperfect preparation of the raw material or defective burning than from incorrect proportions of the constituents. Cement made from very finely ground material, and thoroughly burned, may contain much more lime than the amount usually present and still be perfectly sound. On the other hand, cements low in lime may, on account of careless preparation of the raw material, be of dangerous character. Further, the ash of the fuel used in burning may so greatly modify the composition of the product as largely to destroy the significance of the results of analysis.
- 7. Method. As a method to be followed for the analysis of cement, that proposed by the Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, of the New York Section of the Society for Chemical Industry, and published in the Journal of the Society for January 15, 1902, is recommended.

SPECIFIC GRAVITY.

- 8. Significance. The specific gravity of cement is lowered by underburning, adulteration and hydration, but the adulteration must be in considerable quantity to affect the results appreciably.
- 9. Inasmuch as the differences in specific gravity are usually very small, great care must be exercised in making the determination.

- 10. When properly made, this test affords a quick check for underburning or adulteration.
- 11. Apparatus and Method. The determination of specific gravity is most conveniently made with Le Chatelier's apparatus. This consists of a flask D, Fig. 9, of 120 cu. cm. (7.32 cu. ins.) capacity, the neck of which is about 20 cm. (7.87 ins.)

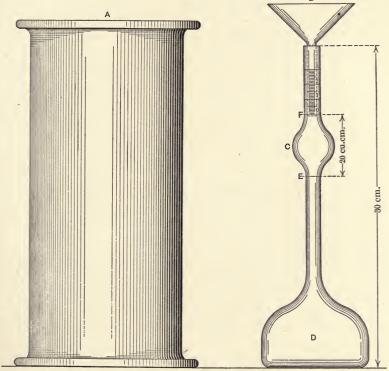


Fig. 9. Le Chatelier's Specific Gravity Apparatus.

long; in the middle of this neck is a bulb C, above and below which are two marks F and E; the volume between these marks is 20 cu. cm. (1.22 cu. ins.). The neck has a diameter of about 9 mm. (0.35 in.), and is graduated into tenths of cubic centimeters above the mark F.

12. Benzine (62 degrees Baumé naphtha) or kerosene free from water should be used in making the determination.

- 13. The specific gravity can be determined in two ways:
- (1) The flask is filled with either of these liquids to the lower mark E, and 64 gr. (2.25 oz.) of powder, previously dried at 100° C. (212° F.) and cooled to the temperature of the liquid, are gradually introduced through the funnel B (the stem of which extends into the flask to the top of the bulb C), until the upper mark F is reached. The difference in weight between the cement remaining and the original quantity (64 gr.) is the weight which has displaced 20 cu. cm.
- 14. (2) The whole quantity of the powder is introduced, and the level of the liquid rises to some division of the graduated neck. This reading plus 20 cu. cm. is the volume displaced by 64 gr. of the powder.
 - 15. The specific gravity is then obtained from the formula:

$$Specific \ Gravity = \frac{Weight \ of \ Cement}{Displaced \ Volume} \cdot$$

- 16. The flask, during the operation, is kept immersed in water in a jar A, in order to avoid variations in the temperature of the liquid. The results should agree within 0.01.
- 17. A convenient method for cleaning the apparatus is as follows: The flask is inverted over a large vessel, preferably a glass jar, and shaken vertically until the liquid starts to flow freely; it is then held still in a vertical position until empty; the remaining traces of cement can be removed in a similar manner by pouring into the flask a small quantity of clean liquid and repeating the operation.
- 18. More accurate determinations may be made with the picnometer.

FINENESS.

19. Significance. — It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses adhesive or cementing qualities. The more finely cement is pulverized, all other conditions being the same, the more sand it will carry and produce a mortar of a given strength.

- 20. The degree of final pulverization which the cement receives at the place of manufacture is ascertained by measuring the residue retained on certain sieves. Those known as the No. 100 and No. 200 sieves are recommended for this purpose.
- 21. Apparatus. The sieves should be circular, about 20 cm. (7.87 ins.) in diameter, 6 cm. (2.36 ins.) high, and provided with a pan 5 cm. (1.97 ins.) deep, and a cover.
- 22. The wire cloth should be woven from brass wire having the following diameters:

No. 100, 0.0045 inch; No. 200, 0.0024 inch.

23. This cloth should be mounted on the frames without distortion; the mesh should be regular in spacing and be within the following limits.

No. 100, 96 to 100 meshes to the linear inch. No. 200, 188 to 200 meshes to the linear inch.

- 24. Fifty grams (1.76 oz.) or 100 gr. (3.52 oz.) should be used for the test, and dried at a temperature of 100° C. (212° F.) prior to sieving.
- 25. **Method.** The committee, after careful investigation, has reached the conclusion that mechanical sieving is not as practicable or efficient as hand work, and, therefore, recommends the following method:
- 26. The thoroughly dried and coarsely screened sample is weighed and placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 200 strokes per minute. The operation is continued until not more than one-tenth of I per cent passes through after one minute of continuous sieving. The residue is weighed, then placed on the No. 100 sieve and the operation repeated. The work may be expedited by placing in the sieve a small quantity of large shot. The results should be reported to the nearest tenth of I per cent.

NORMAL CONSISTENCY.

- 27. Significance. The use of a proper percentage of water in making the pastes * from which pats, tests of setting and briquettes are made is exceedingly important, and affects vitally the results obtained.
- 28. The determination consists in measuring the amount of water required to reduce the cement to a given state of plasticity, or to what is usually designated the normal consistency.
- 29. Various methods have been proposed for making this determination, none of which has been found entirely satisfactory. The committee recommends the following:

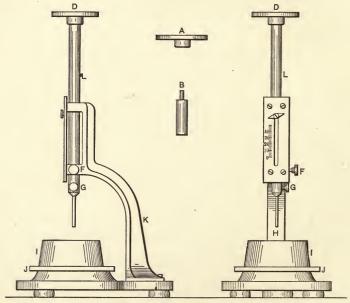


Fig. 10. Vicat Needle.

30. Method. Vicat Needle Apparatus. — This consists of a frame, K, Fig. 10, bearing a movable rod L, with the cap A at one end, and at the other the cylinder B, 1 cm. (0.39 in.) in diameter, the cap, rod and cylinder weighing 300 gr. (10.58 oz.). The rod,

^{*} The term "paste" is used in this report to designate a mixture of cement and water, and the word "mortar" a mixture of cement, sand and water.

which can be held in any desired position by a screw F, carries an indicator, which moves over a scale (graduated to centimeters) attached to the frame K. The paste is held by a conical, hard-rubber ring I, 7 cm. (2.76 ins.) in diameter at the base, 4 cm. (1.57 ins.) high, resting on a glass plate J, about 10 cm. (3.94 ins.) square.

- 31. In making the determination, the same quantity of cement as will be subsequently used for each batch in making the briquettes (but not less than 500 grams) is kneaded into a paste, as described in paragraph 58, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained 6 ins. apart; the ball is then pressed into the rubber ring, through the larger opening, smoothed off, and placed (on its large end) on a glass plate and the smaller end smoothed off with a trowel; the paste, confined in the ring, resting on the plate, is placed under the rod bearing the cylinder, which is brought in contact with the surface and quickly released.
- 32. The paste is of normal consistency when the cylinder penetrates to a point in the mass 10 mm. (0.39 in.) below the top of the ring. Great care must be taken to fill the ring exactly to the top.
- 33. The trial pastes are made with varying percentages of water until the correct consistency is obtained.
- 34. The committee has recommended, as normal, a paste, the consistency of which is rather wet, because it believes that variations in the amount of compression to which the briquette is subjected in molding are likely to be less with such a paste.
- 35. Having determined in this manner the proper percentage of water required to produce a paste of normal consistency, the proper percentage required for the mortars is obtained from an empirical formula.
- 36. The committee hopes to devise such a formula. The subject proves to be a very difficult one, and, although the committee has given it much study, it is not yet prepared to make a definite recommendation.

Note. — The committee on Standard Specifications for cement inserts the following table for temporary use to be replaced by one to be devised by the committee of the American Society of Civil Engineers.

PERCENTAGE OF WATER FOR STANDARD MIXTURES.*

| Neat 18 19 20 21 22 23 24 25 26 27 28 29 30 31 | I-I I2.0 I2.3 I2.7 I3.0 I3.3 I3.7 I4.0 I4.3 I4.7 I5.3 I5.7 I6.0 I6.3 | I-2 IO.0 IO.2 IO.4 IO.7 IO.9 II.I II.3 II.6 II.8 II.80 I2.2 I2.5 I2.7 I2.9 | 9.5 9.7 9.8 10.0 10.2 10.3 10.5 10.7 10.8 11.0 | 8.5 8.7 8.8 8.9 9.1 9.2 9.3 9.5 9.6 9.7 9.9 | 8 8 8 8 8 8 8 9 9 9 | .0 .1 .2 .3 .4 .5 .6 .8 .9 .0 .1 .2 | Neat 33 34 35 36 37 38 39 40 41 42 43 44 45 46 | 1-1 17.0 17.3 17.7 18.0 18.3 18.7 19.0 19.3 19.7 20.0 20.3 20.7 21.0 | 1-2 13.3 13.6 14.2 14.2 14.2 14.3 15.1 15.6 15.6 16.0 | 11.7 11.8 12.0 12.2 12.3 12.5 12.7 12.8 13.0 13.2 13.3 13.5 | 1-4 10.4 10.5 10.7 10.8 10.9 11.1 11.2 11.3 11.5 11.6 11.7 | 10.1 10.2 10.3 10.4 10.5 10.6 10.7 |
|--|---|--|---|---|--|--|--|---|---|--|---|--|
| 32 | 16.7 | 13.1 | 11.3 | 10.3 | | .5 | | | | 3.7 | | |
| | | | | ı to ı | | | to 2 | 1 to 3 | _ _ | 1 to 4 | ı t | 0 5 |
| CementSand | | 500 | | | 333 666 | 250 750 | | 200 800 | | 67 33 | | |

^{*} Revised to 1909.

TIME OF SETTING.

- 37. Significance. The object of this test is to determine the time which elapsed from the moment water is added until the paste ceases to be fluid and plastic (called the "initial set"), and also the time required for it to acquire a certain degree of hardness (called the "final" or "hard set"). The former of these is the more important, since, with the commencement of setting, the process of crystallization or hardening is said to begin. As a disturbance of this process may produce a loss of strength, it is desirable to complete the operation of mixing and molding or incorporating the mortar into the work before the cement begins to set.
- 38. It is usual to measure arbitrarily the beginning and end of the setting by the penetration of weighted wires of given diameters.

- 39. Method. For this purpose the Vicat Needle, which has already been described in paragraph 30, should be used.
- 40. In making the test, a paste of normal consistency is molded and placed under the rod L, as described in paragraph 31, this rod, bearing the cap D at one end and the needle H, 1 mm. (0.039 in.) in diameter, at the other, weighing 300 gr. (10.58 oz.). The needle is then carefully brought in contact with the surface of the paste and quickly released.
- 41. The setting is said to have commenced when the needle ceases to pass a point 5 mm. (0.20 in.) above the upper surface of the glass plate, and is said to have terminated the moment the needle does not sink visibly into the mass.
- 42. The test pieces should be stored in moist air during the test; this is accomplished by placing them in a rack over water contained in a pan and covered with a damp cloth, the cloth to be kept away from them by means of a wire screen; or they may be stored in a moist box or closet.
- 43. Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point reduces the area and tends to increase the penetration.
- 44. The determination of the time of setting is only approximate, being materially affected by the temperature of the mixing water, the temperature and humidity of the air during the test, the percentage of water used, and the amount of molding the paste receives.

STANDARD SAND.

- 45. The committee recognizes the grave objections to the standard quartz now generally used, especially on account of its high percentage of voids, the difficulty of compacting in the molds, and its lack of uniformity; it has spent much time in investigating the various natural sands which appeared to be available and suitable for use.
- 46. For the present, the committee recommends the natural sand from Ottawa, Ill., screened to pass a sieve having 20

meshes per linear inch and retained on a sieve having 30 meshes per linear inch; the wires to have diameters of 0.0165 and 0.0112 inch, respectively, *i.e.*, half the width of the opening in each case. Sand having passed the No. 20 sieve shall be considered standard when not more than one per cent passes a No. 30 sieve after one minute continuous sifting of a 500-gram sample.

47. The Sandusky Portland Cement Company, of Sandusky, Ohio, has agreed to undertake the preparation of this sand and to furnish it at a price only sufficient to cover the actual cost of preparation.

FORM OF BRIQUETTE.

48. While the form of the briquette recommended by a former committee of the Society is not wholly satisfactory,

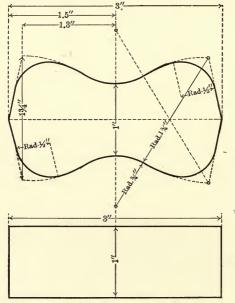


Fig. 11. Details for Briquette.

this committee is not prepared to suggest any change, other than rounding off the corners by curves of one-half inch radius, Fig. 11.

MOLDS.

- 49. The molds should be made of brass, bronze or some equally non-corrodible material, having sufficient metal in the sides to prevent spreading during molding.
- 50. Gang molds, which permit molding a number of briquettes at one time, are preferred by many to single molds, since the greater quantity of mortar that can be mixed tends to produce greater uniformity in the results. The type shown in Fig. 12 is recommended.

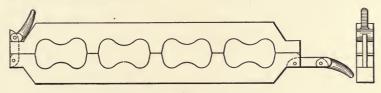


FIG. 12. Details for Gang Mold.

51. The molds should be wiped with an oily cloth before using.

MIXING.

- 52. All proportions should be stated by weight; the quantity of water to be used should be stated as a percentage of the dry material.
- 53. The metric system is recommended because of the convenient relation of the gram and the cubic centimeter.
- 54. The temperature of the room and the mixing water should be as near 21° C. (70° F.) as it is practicable to maintain it.
- 55. The sand and cement should be thoroughly mixed dry. The mixing should be done on some non-absorbing surface, preferably plate glass. If the mixing must be done on an absorbing surface it should be thoroughly dampened prior to use.
- 56. The quantity of material to be mixed at one time depends on the number of test pieces to be made; about 1000 gr. (35.28 oz.) makes a convenient quantity to mix, especially by hand methods.

- 57. The committee, after investigation of the various mechanical mixing machines, has decided not to recommend any machine that has thus far been devised, for the following reasons:
- (1) The tendency of most cement is to "ball up" in the machine, thereby preventing the working of it into a homogeneous paste; (2) there are no means of ascertaining when the mixing is complete without stopping the machine, and (3) the difficulty of keeping the machine clean.
- 58. Method.—The material is weighed and placed on the mixing table, and a crater formed in the center, into which the proper percentage of clean water is poured; the material on the outer edge is turned into the crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by vigorously kneading with the hands for an additional one and one-half minutes, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. During the operation of mixing, the hands should be protected by gloves, preferably of rubber.

MOLDING.

- 59. Having worked the paste or mortar to the proper consistency, it is at once placed in the molds by hand.
- 60. The committee has been unable to secure satisfactory results with the present molding machines; the operation of machine molding is very slow, and the present types permit of molding but one briquette at a time, and are not practicable with the pastes or mortars herein recommended.
- 61. **Method.** The molds should be filled at once, the material pressed in firmly with the fingers and smoothed off with a trowel without ramming; the material should be heaped up on the upper surface of the mold, and, in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the excess material. The mold should be turned over and the operation repeated.

62. A check upon the uniformity of the mixing and molding is afforded by weighing the briquettes just prior to immersion or upon removal from the moist closet. Briquettes which vary in weight more than 3 per cent from the average should not be tested.

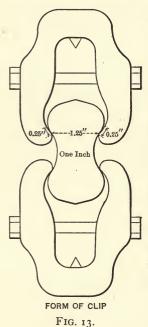
STORAGE OF THE TEST PIECES.

- 63. During the first twenty-four hours after molding the test pieces should be kept in moist air to prevent them from drying out.
- 64. A moist closet or chamber is so easily devised that the use of the damp cloth should be abandoned if possible. Covering the test pieces with a damp cloth is objectionable, as commonly used, because the cloth may dry out unequally, and, in consequence, the test pieces are not all maintained under the same condition. Where a moist closet is not available, a cloth may be used and kept uniformly wet by immersing the ends in water. It should be kept from direct contact with the test pieces by means of a wire screen or some similar arrangement.
- 65. A moist closet consists of a soapstone or slate box, or a metal-lined wooden box the metal lining being covered with felt and this felt kept wet. The bottom of the box is so constructed as to hold water, and the sides are provided with cleats for holding glass shelves on which to place the briquettes. Care should be taken to keep the air in the closet uniformly moist.
- 66. After 24 hours in moist air the test pieces for longer periods of time should be immersed in water maintained as near 21° C. (70° F.) as practicable; they may be stored in tanks or pans, which should be of non-corrodible material.

TENSILE STRENGTH.

67. The tests may be made on any standard machine. A solid metal clip, as shown in Fig. 13, is recommended. This clip is to be used without cushioning at the points of contact with the test specimen. The bearing at each point of contact

should be one-quarter inch wide, and the distance between the center of contact on the same clip should be $1\frac{1}{4}$ inches.



68. Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the briquettes in the testing machine, as cross-strains, produced by improper centering, tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often breaks the briquette before ultimate strength is reached. Care must be taken that the clips and the sides of the briquette be clean and free from grains of sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 pounds per minute. The average of the briquettes of each sample tested should be taken as the test, excluding any results which are manifestly faulty.

CONSTANCY OF VOLUME.

69. Significance. — The object is to develop those qualities which tend to destroy the strength and durability of a cement. As it is highly essential to determine such qualities at once, tests of this character are for the most part made in a very short time, and are known, therefore, as accelerated tests. Failure is revealed by cracking, checking, swelling or disintegration, or all of these phenomena. A cement which remains perfectly sound is said to be of constant volume.

70. **Methods.** — Tests for constancy of volume are divided into two classes: (1) normal tests, or those made in either air or water maintained at about 21° C. (70° F.), and (2) accelerated tests, or those made in air, steam or water at a temper-

ature of 45° C. (115° F.) and upward. The test pieces should be allowed to remain 24 hours in moist air before immersion in water or steam, or preservation in air.

- 71. For these tests, pats about $7\frac{1}{2}$ cm. (2.95 ins.) in diameter, $1\frac{1}{4}$ cm. (0.49 in.) thick at the center, and tapering to a thin edge, should be made upon a clean glass plate about 10 cm. (3.94 ins.) square, from cement paste of normal consistency.
- 72. Normal Test. A pat is immersed in water maintained as near 21° C. (70° F.) as possible for 28 days, and observed at intervals. A similar pat is maintained in air at ordinary temperature and observed at intervals.
- 73. Accelerated Test. A pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel, for three hours.
- 74. To pass these tests satisfactorily, the pats should remain firm and hard, and show no signs of cracking, distortion or disintegration.
- 75. Should the pat leave the plate, distortion may be detected best with a straightedge applied to the surface which was in contact with the plate.
- 76. In the present state of our knowledge it cannot be said that cement should necessarily be condemned simply for failure to pass the accelerated tests; nor can a cement be considered entirely satisfactory, simply because it has passed these tests.

Analysis of Cements. — The following methods of analysis have been suggested by a committee of the New York section, Society of Chemical Industry, consisting of W. F. Hillebrand and Clifford Richardson. For accurate work these methods should be closely followed:

SOLUTION.

One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for 15 minutes, or longer if the blast is not powerful enough to

effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 c.c. of strong HCl added. and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.* The solution is then evaporated to dryness, as far as this may be possible on the bath.

SILICA (SiO₂).

The residue without further heating is treated at first with 5 to 10 c.c. of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for ten minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for fifteen minutes and checked by a further blasting for ten minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 c.c. of HFl and four drops of H₂SO₄ and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.†

^{*} If anything remains undecomposed it should be separated, fused with a little Na_2CO_3 , dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

[†] For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

ALUMINA AND IRON (Al₂O₃ and Fe₂O₃).

The filtrate, about 250 c.c., from the second evaporation for SiO_2 is made alkaline with NH₄OH after adding HCl, if need be, to insure a total of 10 to 15 c.c. strong acid, and boiled to expel excess of NH₃, or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH₄OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted five minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3 + Fe_2O_3^*$.

IRON (Fe₂O₃).

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of KHSO₄, or, better, NaHSO₄, the melt taken up with so much dilute H₂SO₄ that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed and corrected by HFl and H₂SO₄.† The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing CO₂ through the flask, and titrated with permanganate.‡ The strength of the permanganate solution should not be greater than .oo4o gr. Fe₂O₃ per c.c.

^{*} This precipitate contains TiO2, P2O5, Mn3O4.

[†] This correction of $Al_2O_3 + Fe_2O_3$ for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 mg. of SiO_2 are still to be found with the $Al_2O_3 + Fe_2O_3$.

[‡] In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

LIME (CaO).

To the combined filtrate from the Al₂O₃ + Fe₂O₃ precipitate a few drops of NH₄OH are added, and the solution brought to boiling. To the boiling solution 20 c.c. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC₂O₄ assumes a well-defined granular form. It is then allowed to stand for twenty minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. is then ignited, redissolved in HCl, and the solution made up to 100 c.c. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al₂O₃ separates this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed,* weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.†

MAGNESIA (MgO).

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 c.c., 10 c.c. of saturated solution of Na(NH₄)HPO₄ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH₄OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium orthophosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 c.c., 1 c.c. of a saturated solution of Na(NH₄)HPO₄ added,

^{*} The volume of wash-water should not be too large; vide Hillebrand.

[†] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about two hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $\mathrm{Mg_2P_2O_7}$.

ALKALIES (K₂O and Na₂O).

For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of CaCO₃ with NH₄Cl.

ANHYDROUS SULPHURIC ACID (SO₃).

One gram of the substance is dissolved in 15 c.c. of HCl, filtered and the residue washed thoroughly.*

The solution is made up to 250 c.c. in a beaker and boiled. To the boiling solution 10 c.c. of a saturated solution of BaCl₂ are added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as BaSO₄.

TOTAL SULPHUR.

One gram of the material is weighed out in a large platinum crucible and fused with Na₂CO₃ and a little KNO₃, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with HCl and made up to 250 c.c. with distilled water, boiled, the sulphur precipitated as BaSO₄ and allowed to stand over night or for a few hours.

^{*} Evaporation to dryness is unnecessary, unless gelatinous silica should have separated, and should never be performed on a bath heated by gas; *vide* Hillebrand.

LOSS ON IGNITION.

Half a gram of cement is to be weighed out in a platinum crucible, placed in a hole in an asbestos board so that about three-fifths of the crucible projects below, and blasted fifteen minutes, preferably with an inclined flame. The loss by weight, which is checked by a second blasting of five minutes, is the loss on ignition.

May, 1903: Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should, therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

Summary and Conclusions. - In Chapters III and IV the inorganic dust layers and road binders have been considered in some detail, both as regards their chemical and physical characteristics, methods of application and examination. The materials have been discussed in the order of their binding value from water alone, the poorest, to Portland cement, the most powerful binder. A significant fact to be noted is that all of these materials are dependent for their binding value upon the presence or action of water. In the former case water produces a weak physical bond, but in the latter often a very powerful chemical bond due to the formation of hydrated compounds. Certain salts such as sodium silicate and bases such as quicklime may increase the action of water upon road materials, but they are inert if water is not present. The position of stone screenings, rock dust and clays is shown to be among the semipermanent binders and the action of water upon the two former somewhat analogous to its action upon hydraulic cements. A connecting link between the two would seem to exist in the reactions which take place between water and certain kinds of slag powders. The advantages of employing hydraulic cements as binders for foundation courses have been particularly emphasized and their suitability for wearing surfaces discussed.

CHAPTER V.

ORGANIC NON-BITUMINOUS DUST PREVENTIVES AND ROAD BINDERS,

Organic non-bituminous materials constitute the least important class of dust preventives and road binders. They have for the most part been employed to a very limited extent except perhaps in patented preparations in combination with other materials of varying character. In general they may be said to include certain vegetable and animal oils of little value, other than as dust layers; waste products from such sources as wood pulp mills and sugar refineries, which may be considered as semipermanent binders; and compounds of rosin or resinic acids with inorganic bases, which are perhaps more lasting in their effect and may be considered as permanent binders. Most of these materials have been employed in only a few isolated experiments so that but little reliable data are to be had as to the best method of applying them, and their comparative value as binders under varying con-Their use has ordinarily been confined to localities near which they are produced, although the fact that some of them are waste products, and therefore cheap, should place them in competition with the other classes of materials in certain instances, and widen their sphere of usefulness.

Vegetable Oils. — Vegetable oils as a class can only be considered as dust layers and temporary binders, as they contain little or no true binding base, but are dependent upon their moistening or oiling effect to hold the dust particles together. Their action is, in this respect, precisely the same as that of water, but the results are of a more lasting character as the oils are less volatile than water, and, therfore, remain upon the road for a longer time and prove effective until they have become saturated with dust. Their binding value or lack of binding value

may be readily demonstrated by making up rock dust briquettes in which the oil is substituted for water and subjecting them to the cementation test described on page 64. As a typical example of the effect of vegetable oils when used on roads, may be mentioned an experiment with oil of aloes tried in Algiers a few years ago. The oil was sprinkled upon the surface of the road in its natural condition for the purpose of laying dust. It was found that the dust was well laid for a considerable length of time by this means, but that in wet weather an oily, slippery mud was produced which was so disagreeable that use of the oil for this purpose was abandoned.

Cotton seed oil has been employed to some extent in road preparations, mainly saponified with an alkali to produce a soap solution capable of acting as an emulsifying agent for mineral oils and tars. Linseed oil and rosin oil have also been suggested, the latter forming compounds which have more or less binding value. One patent calls for the addition of glue and bichromate of potash to an oil preparation, which is supposed to cause it to harden upon the road surface under the action of light. Such a preparation is sold in England under the name of Crempoid D. These substances are mentioned not because of their value as binders, but merely to show the variety of materials which have been suggested or tried. The principal value of vegetable oils and also of animal oils would seem to lie in their use in connection with saponifying materials for the purpose of making emulsions of the true binding bituminous oils. Such emulsions will be taken up in a later chapter.

Animal Oils and Fats. — The same objections that have been made to the use of vegetable oils are applicable to animal oils and fats. Such materials carry no true binding base, and while they are excellent dust layers the mud which they produce in wet weather is so objectionable as to have discredited their use except in the production of soaps for the purpose described above.

A Scotch preparation, known as "Sandisize," which has been patented both in England and this country,* deserves mention

^{*} U. S. Patent No. 813,389. Feb. 20, 1906.

as having been employed with fairly good results as a dust layer. This material is prepared from a by-product obtained from wool scourings after most of the wax has been extracted.

Before raw wool can be subjected to any manufacturing process it must be washed and scoured to remove impurities, which are present to the extent of from 30 to 80 per cent of the total weight. These impurities consist of yolk or wool grease; suint, composed mainly of potassium salts of oleic, stearic, valeric and acetic acids, together with sulphates, chlorides, phosphates and nitrogenous bodies; and dirt which is mechanically entangled among the fibers. These substances can be removed by washing the wool in a solution of soap. Wool is often treated to recover the yolk and suint separately, accomplished by first extracting it with a volatile solvent to remove the former and then washing it to dissolve and remove the suint and dirt. It is the latter product which is mainly employed in the manufacture of Sandisize, and to it is added caustic potash or potassium carbonate and an oil of disinfectant properties, such as creosote oil. This material is concentrated and sold as a dust preventive. It is applied to the road surface in diluted form by means of a sprinkler. In Scotland the cost of treating one mile of sixteen-foot roadway with a-10 per cent solution, is about \$21.50. It is stated that three or four applications per season will effectively lay the dust for that length of time. Four such treatments would, therefore, average less than one cent per square yard, which is exceedingly cheap. The number of treatments necessary will, however, vary with local conditions so that in some cases the cost would be higher. To the author's knowledge this material has not as yet been employed in this country. In Scotland, where it has been most extensively used, it is sold in concentrated form for about \$30.00 per ton.

Waste Sulphite Liquor. — In the manufacture of wood pulp, according to the sulphite process, a waste liquor is produced in large quantities, which in its original condition is not only of no value, but a nuisance to localities near which it is pro-

duced. In the sulphite process wood is boiled under pressure in a digester with sulphurous acid or more commonly with an acid sulphite, of calcium and magnesium. By the action of these chemicals the lignin and other incrusting matters of the wood fiber are broken down into complex substances largely soluble in water. Their exact composition is not known, but for want of a better name they have been called calcium or magnesium ligno-sulphonates. The solution thus produced is known as waste sulphite liquor and is usually allowed to run to waste in some near-by stream where it pollutes the water, kills fish and is a source of danger and annoyance.

Crude waste sulphite liquor is a thin, light brown liquid, of slightly acid reaction and having a specific gravity of from 1.03 to 1.05. If it is evaporated nearly to dryness, a gummy residue is obtained, and this fact has suggested its use as a binding medium. While the crude liquor has little or no binding value, concentrated liquors exhibit this property to a marked extent and recently an attempt has been made to employ them as dust layers and road binders. In fact, a road preparation containing this binding medium is now on the market under the name of Glutrin. This material has a specific gravity of about 1.26 or 1.27 which represents a concentration of the crude material to about one-fifth of its original volume. Before application it is diluted with an equal quantity of water which produces a solution having a specific gravity of 1.13.

The cementing value developed by such solutions when mixed with rock powders is shown in the following table. In this table is given the cementing value of various rock powders with water alone as compared with their cementing value when treated in the same manner and with the same amount of Glutrin and other concentrated sulphite liquors having a specific gravity of 1.13. For a description of the cementing value test, see page 64. The crushing strength of the briquettes, as made for the cementing value test and determined by means of a small Olsen testing machine in the usual manner, is also included in this table for the purpose of comparison.

| Roc No. | k Sample. | . Mixed with. | Cementing Value. | Crushing Strength, (1bs.) |
|------------------------------|-------------------------------|--------------------------------|----------------------|---------------------------------|
| 2900 2900 2900 2900 | Trap. Trap. Trap. Trap. Trap. | Water alone | 11 1000+ 1000+ | 368 2477 2100 2450 |
| 2901 | Gneiss. | Water alone | 27 | 415 |
| 2901 | Gneiss. | | 1000+ | 2840 |
| 2901 | Gneiss. | | 800 | 2360 |
| 2901 | Gneiss. | | 1000+ | 2200 |
| 2971 | Sandstone. | Concentrated sulphite liquor A | 10 | 340 |
| 2971 | Sandstone. | | 800+ | 2258 |
| 2971 | Sandstone. | | 400 | 2260 |
| 2971 | Sandstone. | | 690 | 2250 |

From these results it will be seen that concentrated sulphite liquors act as powerful road binders. As the binding base is, however, soluble in water, it is evident that frequent rains will tend to destroy the bond and remove the material from the road surface. This is demonstrated by the fact that rock dust briquettes in which they are employed slake quite readily when immersed in water.

In order to overcome this difficulty, attempts have been made to incorporate with the sulphite liquor some material which after it has dried out upon the road will waterproof or make insoluble the residual base, without destroying its binding value. The best results along this line have been obtained by the use of from 5 to 15 per cent of a semiasphaltic road oil, showing the following characteristics:

SEMIASPHALTIC OIL.

| Specific gravity 25°/25° C | .948 |
|--|--------|
| Flash point ° C | 197 |
| Loss at 163°C, 5 hours | 2.80% |
| Material soluble in carbon bisulphide, total bitumen | 99.4 % |
| Bitumen insoluble in 86° paraffin naphtha | 1.50% |
| Fixed carbon | 1.45% |

It was found that such an oil could be readily mixed or emulsified with the sulphite liquor and, when employed in the quantities stated, that the binding base was made almost insoluble after it had once dried out. While rock dust briquettes made with these mixtures showed no depreciation in cementing value when tested dry, and while they did not slake, it was noticed that they became somewhat soft after immersion in water over night. Oil sulphite liquor mixtures would therefore seem to be unsatisfactory as road binders in wet weather, if applied to a road having much fine material upon its surface. It may be added that the use of such mixtures has been patented * as also mixtures of waste sulphite liquor with deliquescent salts such as calcium chloride.

As has been stated, crude waste sulphite liquors have but little binding value, and when applied to road surfaces are hardly more efficient as dust layers and road binders than water alone. Their use is, however, covered by patent.†

From experiments which have come under the author's notice, it would seem that concentrated waste sulphite liquors are suitable for use only upon macadam or similar roads. When subjected to favorable conditions, they may be considered as semipermanent binders, although more than one application will ordinarily have to be made in order to lay the road dust for one season. If of the specific gravity mentioned, 1.26, they should be diluted with an equal volume of water and applied to the road surface by means of a sprinkling cart at the rate of o.6 gallon solution, or 0.3 gallon of the original material per square yard. Before application the road should be swept clean if much dust is present, or otherwise the solution will not be absorbed by the road proper, but by the dust, forming a hard cake, which is likely to scale off in dry weather. If the road surface is fairly clean, however, it will readily absorb the material which, upon drying out, binds the roadstones firmly together until eventually removed by rains. A road so treated is usually slightly darkened in color and presents a hard compact surface.

^{*} U. S. Patent No. 865,578, Sept. 10, 1907.

[†] U. S. Patent No. 781,079, Jan. 31, 1905.

Additional treatment will be required from time to time, depending upon local conditions, and when made should consist of an application of not over 0.1 or 0.2 gallon of the original material per square yard, made in suitable dilution. It will be found that results of similar duration to the first treatment will be obtained by such applications.

Glutrin, which has already been mentioned, is the only waste sulphite liquor preparation that has been employed to any extent in this country as a dust preventive and road binder. It can at present be purchased at from twelve to fifteen cents per gallon f.o.b. at point of storage, depending upon the quantity ordered and whether shipped in barrels or tank car. Taking the minimum figure it can, therefore, be seen that application made in the manner above described will cost for material alone, excluding freight, not less than four cents per square yard for the first treatment and not less than 1.3 cents per square yard for each succeeding application.

Molasses Residues. — In the manufacture of sugar from sugar cane a by-product is obtained which is known as black strap, or waste molasses. This molasses is a very thick syrupy liquid, from which all of the commercially removable sugar has been extracted. It contains resinous and inorganic constituents which make it unfit for culinary purposes. A small amount is used for feeding cattle, and some in the manufacture of rum, but it is employed mostly as a fuel. In the neighborhood of sugar factories it has in some instances been experimentally employed as a binder for cinder paths and roads. When treated with quicklime, molasses forms compounds of high binding value known as calcium sucrates. Those sucrates are, however, soluble in water and should, if possible, be waterproofed before being employed as road binders. Working along this line the * United States Office of Public Roads conducted an experiment at Newton, Massachusetts, during the summer of 1908, with a molasses, lime, oil mixture as a road binder. A description of this experiment is given below as being the only authentic report of the

^{*} Circular No. 90, Office of Public Roads, U. S. Dept. of Agriculture.

use of molasses as a road binder. While the results obtained have up to the date of publication of this book proved quite satisfactory, too short a time has elapsed to warrant any definite assertion being made as to the value of such a mixture as a permanent binder. In any event, however, it would seem that in certain localities, preferably dry, where molasses may be obtained at low cost, it might be satisfactorily employed in dilution as a dust layer. Waste molasses from beet sugar refineries should also prove serviceable for this purpose.

In the molasses, oil, lime experiment referred to, the binder was prepared in a large mortar box by first slaking 320 pounds of quicklime with 108 gallons of water. As soon as the lime was completely slaked, 92 gallons of molasses were added and thoroughly mixed with it, after which 50 gallons of a semi-asphaltic oil showing the following analysis were stirred in.

SEMIASPHALTIC OIL.

| Specific gravity 25°/25° C | 0.994 |
|--|-----------|
| Flash point degrees C | 245 |
| Volatilization tests, | |
| Loss at 100° C., 5 hours | 0.25% |
| Loss at 163° C., 7 hours | 0.85% |
| Loss at 204° C., 7 hours | 5.30% |
| Residue | 94.70% |
| Character of residueSoft semiasphaltic, pulled | to thread |
| Material soluble in carbon bisulphide, total bitumen | 99.85 |
| Organic matter insoluble | .15 |
| Inorganic matter | 0.00 |
| | |
| | 100.00 |
| Bitumen insoluble in 86 degrees naphtha | 5.45% |

While the preparation was still hot it was mixed on a board with cold stone in the proportion of 18 gallons of the preparation to 960 pounds of $\frac{1}{2}$ -inch to $\frac{3}{4}$ -inch stone to 350 pounds of $\frac{3}{4}$ -inch stone running to dust, just as it came from the crusher. The concrete thus produced was hauled to the road and laid upon a prepared broken stone foundation as soon after mixing as possible. It was applied to a finished depth of two inches and after rolling produced a firm, resilient surface upon which heavily

loaded wagons produced no wheel marks one-half hour after it was laid. Under the action of the roller a small portion of the oil came to the surface, so that a light application of stone chips was required to put the surface in good condition. The labor item was exceedingly high in this experiment, because of the inexperience of the workmen in preparing and handling the material. The total cost per square yard in excess of ordinary macadam work of the same nature was about twenty-two cents.

Rosin and Resinates. — Some tendency has been shown in patent preparations to make use of rosin as a binding medium. When dissolved in or combined with various oils, it produces very sticky compounds some of which may be applied in the form of emulsions. It may be remarked that compounds of rosin with lime or iron have been employed to some extent in the manufacture of artificial stone. These compounds are known as resinates of the inorganic bases which they contain, and at the present time are of interest only in regard to their possible use as permanent road binders. Where rosin has been employed as a road binder, it has invariably been combined with other materials so that it is hardly possible to consider its application and use as an individual substance.

Summary and Conclusions. — In this chapter a number of organic non-bituminous materials have been considered with reference to their use as dust layers and road binders. Of these, waste sulphite liquor is probably the most important, owing to the fact that from the ordinary standpoint it is an undesirable product found in various localities throughout this country, and should be quite generally available at small cost. Other materials such as vegetable and animal oils will never be employed to any great extent for this purpose and are relatively unimportant. Their chief value seems to lie in their soap making property when treated with caustic alkalies, the soaps so obtained being employed as emulsifying agents for true binding bituminous materials.

CHAPTER VI.

HYDROCARBONS.

The most important types of dust preventives and road binders are undoubtedly to be found among the large and varied class of substances known as bitumens, and before taking up the various members separately with relation to their dust laying and road binding properties, it seems necessary for a proper understanding of the subject to briefly consider their chemical composition and constitution. In a single chapter this can be done only in a very general way, as the compounds found in coal tar and petroleum, together with their derivatives, constitute the greater part of our present organic chemistry.

Bitumens as a class are composed mainly of compounds of carbon and hydrogen, known as hydrocarbons, together with smaller amounts of their oxygen, nitrogen and sulphur derivatives. The character of the hydrocarbons themselves determines, to a great extent, the physical properties of the bituminous materials, and some knowledge of the various classes of hydrocarbons is, therefore, essential. Only the typical and most important members of each class can here be described, but it is believed that this will enable the reader to obtain a fair idea of the subject as a whole and to appreciate and understand the differences in properties of the various bituminous road materials which will be more fully discussed in later chapters.

The Carbon Atom. — Carbon is known as a quadrivalent element; that is, its atom has four valences or unsatisfied affinities ready to unite with other atoms or radicals to form compounds. It is commonly represented by the letter C surrounded by four dashes, each dash denoting a valence:

The carbon atom is capable of combining with hydrogen under favorable conditions to form a hydrocarbon molecule or compound. As hydrogen (H) is a monovalent element, having but one combining link or valence, and as all of the valences in a molecule must be satisfied by union with the valences of other atoms, it is evident that four hydrogen atoms are required to satisfy the carbon atom and that the compound thus produced must have the formula CH₄. This may be considered as the parent hydrocarbon, and may be graphically expressed as follows:

Besides its ability to combine with hydrogen the carbon atom can unite with other carbon atoms and it may do this in three ways, either by a single, double or triple linkage, as follows:

The remaining valences may then be taken up by hydrogen atoms to form the corresponding hydrocarbons, C_2H_6 , C_2H_4 , C_2H_2 .

Instead of hydrogen atoms, other carbon atoms may be taken up in an almost limitless number and according to any of the three methods of linkage made possible by the free valences present. Thus we may have

When the linkage of carbon atoms is open at both ends, as in the preceding examples, the compounds are known as open chain hydrocarbons. The carbon atoms may, however, be joined together so as to form a closed chain or ring, in which case they are called cyclic hydrocarbons. Examples of the more simple ring compounds are as follows:

In the ring compounds, as in the open chain compounds, the carbon atoms may be united by a double as well as a single bond. In either class when the bonds are all single the compound is said to be saturated. When a double or triple union occurs, however, the compound is called unsaturated, because the extra valences between the carbon atoms are not taken up by other atoms. The unsaturated compounds are as a rule less stable chemically than the saturated, and many of them are capable of reacting with various substances in such a way as to break down the double or triple bond and form saturated compounds.

In the study of organic chemistry, it is customary to separate the hydrocarbons into two main classes: (1) open chain and (2) cyclic; and to subdivide each of these classes into two groups; (a) saturated, and (b) unsaturated. This method will be adhered to in the following brief consideration of those hydrocarbons which are of typical occurrence in bituminous road binders.

I. OPEN CHAIN HYDROCARBONS.

(a). Saturated. — The saturated open chain hydrocarbons are commonly known as paraffins. They constitute a series of compounds the simplest member of which is CH_4 , which has already been mentioned. This compound is known as methane or marsh gas. The next member, C_2H_6 , is known as ethane, the third, C_3H_8 , as propane, the fourth, C_4H_{10} , as butane, the fifth,

 C_5H_{12} , as pentane, etc. It will be noticed that each member differs from the preceding member by CH_2 . In other words, they constitute an homologous series with a constant difference of CH_2 , and their general formula may be expressed as $C_nH_{2^{n+2}}$. By a glance at the following graphic formulæ it will also be seen that each succeeding member may be considered as formed from the preceding member by the replacement of one of its hydrogen atoms by CH_3 . Thus:

 $\mathrm{CH_3}$ can, therefore, be considered as a radical, or group of atoms corresponding to an atom with a single valence. In like manner $\mathrm{CH_2}$ can be considered as a bivalent radical and CH as trivalent. These radicals derive their names from the parent hydrocarbon, methane, and similar radicals are derived from the other members of the series. Thus:

| Methane. | Methyl. | Methylene. | Methenyl. |
|----------|--------------------|------------|-----------------|
| CH_4 | $-\mathrm{CH_3}$ | $=CH_2$ | ≡CH |
| Ethane. | Ethyl. | Ethylene. | Ethenyl. |
| C_2H_6 | $-\mathrm{C_2H_5}$ | $=C_2H_4$ | $\equiv C_2H_3$ |
| Propane. | Propyl. | Propylene. | Propenyl. |
| C_3H_8 | $-C_3H_7$ | $=C_3H_6$ | $\equiv C_3H_5$ |

If the number of carbon atoms in the open chain compounds is greater than three, their relative position to one another may vary so as to produce different compounds having the same number of carbon and hydrogen atoms, but differing somewhat in their chemical and physical properties. Such compounds are known as isomers. Thus C₄H₁₀ may exist in two modifications as shown by the formulas,

In the latter case a side chain is introduced and the relative position of the carbon atoms changed.

It is evident that as the number of carbon atoms increases, the number of possible isomers increases rapidly. Thus three isomers are possible for pentane (C_5H_{12}) :

$$\begin{array}{c} \text{CH}_3\\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3\\ \text{Normal pentane.} \end{array} \\ \begin{array}{c} \text{CH}_3\\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3\\ \text{Iso pentane.} \end{array} \\ \\ \begin{array}{c} \text{CH}_3\\ \text{CH}_3-\text{C}-\text{CH}_3,\\ \\ \text{CH}_3\\ \end{array} \\ \\ \begin{array}{c} \text{CH}_3\\ \end{array} \\ \\ \text{Tetra Methyl Methane.} \end{array}$$

The next member, hexane (C_6H_{14}) , has 6 isomers, while tridecane $(C_{13}H_{28})$ has 802 isomers. It is thus seen that the number of different paraffin hydrocarbons is enormous. The known normal paraffins alone run as high as $C_{00}H_{122}$, and the possible isomers for this compound are almost beyond comprehension, except in a comparative way. Some idea can, therefore, be obtained at this point of the futility of attempting to determine the presence of isolated compounds in bituminous road materials which are themselves extremely complex mixtures of the paraffin and various other hydrocarbon series in varying proportions. The presence and especially the predominance of

certain series can, however, be ascertained either directly or indirectly, and this is often a valuable aid in determining the road building properties of the material.

The lowest members of the paraffin series up to C_4H_{10} are gases at ordinary temperature, and, therefore, need not be considered in relation to road preparations. The intermediate members, from C_5H_{12} to $C_{15}H_{32}$, are colorless oily liquids, and the higher members, beginning with $C_{16}H_{34}$, are greasy crystalline solids.

The melting and boiling points of the known normal paraffins from pentane up, as given by Richter,* are shown in the following table. It should be noted that the higher members from $C_{20}H_{42}$ up are only volatile, without decomposition, under reduced pressure.

| Name | Formula. | Melting Point, Degrees C. | Boiling Point, Degrees C. |
|--|---|--|---|
| Pentane Hexane Heptane Octane. Nonane Decane Undecane Dodecane Tridecane Tetradecane Hexadecane Heyadecane Heradecane Totadecane Tridecane Tritadecane Heradecane Heradecane Heradecane Heptadecane Tricosane Heneicosane Tricosane Heneicosane Docosane Tricosane Heptadecosane Heptadecane Portacosane Heneicosane Heneicosane Tricosane Heptacosane Heptacosane Heptacosane Heptacosane Heptacosane Heptacosane Heptacosane Heptacosane Hentriacontane Dotriacontane Pentatriacontane | $\begin{array}{c} C_5H_{12} \\ C_6H_{14} \\ C_7H_{16} \\ C_8H_{18} \\ C_9H_{20} \\ C_{10}H_{22} \\ C_{11}H_{24} \\ C_{12}H_{36} \\ C_{12}H_{36} \\ C_{13}H_{28} \\ C_{14}H_{30} \\ C_{15}H_{32} \\ C_{16}H_{32} \\ C_{16}H_{32} \\ C_{16}H_{32} \\ C_{16}H_{33} \\ C_{17}H_{36} \\ C_{18}H_{38} \\ C_{19}H_{44} \\ C_{29}H_{44} \\ C_{29}H_{44} \\ C_{22}H_{46} \\ C_{23}H_{48} \\ C_{24}H_{50} \\ C_{27}H_{44} \\ C_{27}H_{46} \\$ | -51 -32 -26.5 -12 -6.2 +5.5 10 18 22.5 28 32 36.7 40.4 44.4 47.7 51.1 59.5 68.1 70.0 74.7 | 38 71 98.4 125.5 149.5 149.5 124.5 214 252.5 2270.5 287.5 303 317 339 205 224.5 234 243 270 302 310 331 331 331 331 331 331 331 |

^{* &}quot;Richter's Organic Chemistry" (Smith), 3d Ed., Vol. 1, p. 86. Blackiston's Sons & Co.

All of the paraffin hydrocarbons are insoluble in water. The lower and intermediate members are readily soluble in alcohol and ether, but the higher members are less soluble, especially at low temperatures, and this fact has been made the basis of a determination for paraffin scale which will be described in a later chapter.

Liquid paraffins may be separated from hydrocarbons of most of the other series by treatment with sulphuric acid as long as the acid becomes colored and then with fuming nitric acid. Other substances are oxidized or converted into compounds which are dissolved by the acids while the paraffins remain unaltered and may be separated by suitable means.

The paraffin hydrocarbons occur principally in petroleum, although they are also found to some extent in the products of destructive distillation. They are for the most part undesirable constituents when present in large quantities in road binders, as will appear later.

(b). Unsaturated. — The unsaturated open chain compounds may be divided into two main classes. (1) those containing two carbon atoms doubly linked, and (2) those containing two carbon atoms trebly linked. The former are known as olefines and the latter as acetylenes. Both constitute an homologous series with a constant difference of CH₂ between adjoining members as in the paraffin series. Other series containing two double linkages, known as diolefines, and two treble linkages, known as diacetylenes, likewise exist, but need not be considered separately. Compounds with both double and treble linkages are also known and these are called olefinacetylenes.

Olefines. — The first member of the olefine series, C_2H_4 , is ethylene, the second, C_5H_6 , propylene, the third, C_4H_8 , butylene. They may be graphically expressed as follows and it will be seen, as in the case of the paraffins, that each member may be considered as formed from the preceding one by the replacement of one of its hydrogen atoms by the radical CH_3 .

$$\mathrm{CH_2} = \mathrm{CH_2}$$
 $\mathrm{CH_2} = \mathrm{CH} \cdot \mathrm{CH_2}$ $\mathrm{CH_2} = \mathrm{CH} \cdot \mathrm{CH_2} \cdot \mathrm{CH_3} \cdot \mathrm{CH_3}$.

Ethylene Propylene Butylene

The general formula for this series of hydrocarbons is C_nH_{2n} .

Beginning with butylene, isomers are encountered and for the formula C₄H₈ we may have

For the higher members a rapidly increasing number of isomers exists. The first three members of the ethylene series are gases at ordinary temperatures, the intermediate members liquids and the higher members solids. The boiling points of the known olefines which have been shown by Shorlemmer to exist in American petroleums are given in the following table. Some of these are also found in coal tars and oil tars.

| Name. | Formula. | Boiling Point, Degrees C. |
|---|--|---|
| Gaseous. Ethylene Propylene Butylene | $C_{2}H_{4} \\ C_{3}H_{6} \\ C_{4}H_{8}$ | -18 +3 |
| Fluid. Amylene Hexylene Heptylene Octylene Nonylene Decatylene Endecatylene Dodecatylene Decatritylene Cetene | $C_{6}H_{12}$ $C_{7}H_{14}$ $C_{8}H_{16}$ $C_{9}H_{18}$ $C_{10}H_{20}$ | 35 69 95 104 140 160 195 216 235 275 |
| Solid. Cerotene | $\begin{array}{c} C_{27}H_{54} \\ C_{30}H_{60} \end{array}$ | 375 |

In chemical properties the olefines differ greatly from the paraffins. Concentrated sulphuric acid absorbs them, forming ethereal salts and other addition products, and this reaction can be used to separate them from the paraffins. In themselves they are probably of little value when present in road binders, but if found in appreciable quantities are indicative of at least an approach towards suitable road binders. They are of peculiar interest in respect to their relation to the saturated ring hydrocarbons of like carbon contents, known as naphthenes, which have the same general formula and may therefore be considered as their isomerides.

Acetylenes. — The acetylene series takes its name from the first of its members, C_2H_2 . Each member following differs from the preceding by CH_2 and the general formula for this series is, therefore, $C_nH_{2^{n-2}}$. Thus:

$$\begin{array}{lll} {\rm CH} \equiv {\rm CH} & {\rm CH} \equiv {\rm C-CH_3} & {\rm CH_3-C} \equiv {\rm C-CH_3}. \\ & {\rm Alctylene.} & {\rm Crotonylene.} \end{array}$$

Isomeric modifications begin with crotonylene, the third member. The following table gives the boiling points of some of the acetylenes.

| Name. | Formula. | Boiling Point, Degrees C. |
|---|---|--|
| Acetylene. Allylene. Crotonylene Ethyl acetylene. Methyl ethyl acetylene. Normal propyl acetylene Isopropyl acetylene | $CH \equiv CH$ $CH_3C \equiv CH_3$ $CH_3C \equiv C \cdot CH_3$ $C_2H_5C \equiv CH$ $C_2H_5C \equiv C \cdot CH_3$ $C_3H_7C \equiv CH$ $(CH_3)_2CH \cdot C \equiv CH$ | Gas. Gas. 27-28 18 55-56 48-49 28-29 |

While acetylenes are found to a limited extent in some classes of petroleum, their presence in tars is of more interest in relation to their close connection with the formation of the benzene series of hydrocarbons which are unsaturated ring compounds having an entirely different general formula.

Thus at high temperatures three molecules of C₂H₂ may polymerize to form a single molecule of C₆H₆, benzene, which

will be described later under another series of hydrocarbons. Polymerism may be considered as isomerism of bodies of different molecular mass, or the aggregation of two or more like molecules into a new molecule. Members of many of the series of hydrocarbons are known to polymerize under favorable conditions. Paraffin hydrocarbons, however, cannot polymerize, as has been proved by Mayberry, for a multiple of any compound having the formula $C_nH_{2^{n+2}}$ would no longer preserve the ratio of carbon to hydrogen observed among the paraffins.

II. CYCLIC HYDROCARBONS.

(a). Saturated.—The saturated cyclic hydrocarbons are known as polymethylenes. The bonds between the adjacent carbon atoms are of course single. The polymethylenes may most conveniently be considered under two divisions according to their structure, (1) those which consist of one cycle only, and (2) those consisting of more than one cycle. The former are called naphthenes, or monocyclic polymethylenes, and the latter polycyclic polymethylenes. The monocyclic polymethylenes constitute an homologous series, the dicyclic another, the tricyclic a third, etc. They are found particularly in oils of asphaltic characteristics and in the solid native bitumens.

Naphthenes. — While the simple monocyclic polymethylenes may be composed of any number of methylene (CH₂) radicals, from three to seven united in a single ring, it is to the hexamethylenes, or hexahydrobenzenes as they are often called, that the term naphthenes is mainly applied. The first member of the naphthene series is hexamethylene (C_6H_{12}), and the other members may be considered as being formed from it by the replacement of one or more of its hydrogen atoms by CH₃ or other open chain radicals. It is isomeric with methyl pentamethylene, as shown below.

The next two members may be represented as follows, and are seen to consist of a single ring radical in combination with an open chain radical.

$$\begin{array}{c} \operatorname{CH_2} \cdot \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{Methyl} \ \operatorname{Hexamethylene} \ \operatorname{or} \\ \operatorname{Hexahydrotoluene} \end{array} \quad \begin{array}{c} \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{CH_2} \cdot \operatorname{CH_2} \\ \operatorname{Ethyl} \ \operatorname{Hexamethylene} \ \operatorname{or} \\ \operatorname{Hexahydroxylene} \end{array}$$

The constant difference CH_2 exists between the adjacent members, and the general formula is, therefore, C_nH_{2n} which is the same as that of the olefines.

Isomers of many of these members have been isolated and the number of possible isomers is almost limitless. The boiling points of the first nine members and some of their isomers, as given by Markownikoff,* are shown in the following table. These hydrocarbons have been isolated from certain types of petroleums.

| Name. | Formula. | Boiling Point, Degrees C. |
|--|--|--|
| Hexahydrobenzene Hexahydrotoluene Hexahydro-m-xylene. Hexahydromesitylene Hexahydro-\psi-cumene Hexahydropropylbenzene. Dodecahydronaphthalene | $\begin{array}{c} C_{6}H_{12}.\\ C_{7}H_{14}\\ C_{8}H_{16}.\\ \\ C_{9}H_{18}.\\ \\ C_{10}H_{20}\\ C_{11}H_{22}\\ C_{12}H_{24}\\ C_{14}H_{28}\\ C_{15}H_{30}\\ \end{array}$ | 69 95-98 115-124 135-138 135-138 140-142 153-170 179-181 197 240-241 246-248 |

Although not as stable as the paraffin hydrocarbons, the naphthenes are not acted upon by sulphuric acid. The higher members are, however, more reactive than the lower. They do not solidify at low temperatures and are separated from the paraffins by freezing and filtration. The naphthenes are found principally in Russian petroleum, although they exist to some extent in American petroleums as well as tars.

^{*} Jurn. Russk. Ph.-Kh. Obsch., XV, 237 (1883), and XXIV, 141 (1892).

Polycyclic Polymethylenes. — In the polycyclic polymethylenes two or more rings are found which have a number of carbon atoms common to both. Examples of this are shown by the following known compounds, which are said to have a bridge structure.

Both of these hydrocarbons belong to the C_nH_{2n-2} series of saturated compounds. But little is known of the various members of this and many other series of polycyclic polymethylenes and their constitution is largely a matter of theory. They may in general be said to occur in petroleums of an asphaltic nature and in the native asphalts. The higher members are extremely complex.

(b). Unsaturated. — There are quite a large number of unsaturated cyclic hydrocarbon series, but only three, which are of the most importance in the study of road binders, will be taken up in any detail. The nucleus of these hydrocarbons, which are known as the benzene, the naphthalene and the anthracene series, is the benzene ring, which consists of six carbon atoms joined together with alternate single and double linkages as shown:

Each carbon atom has one free valence which may be taken up by hydrogen or various univalent radicals. In spite of the fact that three double linkages are present, this ring is comparitively stable and remains intact during most reactions. Under suitable conditions it can, however, be broken down to the saturated hexahydrobenzene nucleus which has been encountered under the naphthenes.

Benzene Series. — The first member of the benzene series is benzene (C_8H_8) or benzol as it is often called. The next member is toluene (C_7H_8) , and the third xylene (C_8H_{10}) . They may be graphically expressed as follows:

The constant difference CH_2 is found between the members of this series whose general formula is C_nH_{2n-6} . Beginning with xylene, isomers are encountered, there being four for this compound. Thus the formula given above is that representing orthoxylene, which is a dimethyl benzene. The other three are as follows:

Benzene (C_6H_6) is the parent hydrocarbon of the so-called aromatic compounds. It is a mobile ethereal liquid with a characteristic odor, having a definite boiling point. It should not be confused with benzine, which is the term applied to the lighter and more volatile fractions of petroleum, consisting mainly of the paraffin series. The melting and boiling points of some of the most important members of the benzene series are given in the following condensed table taken from Richter's Organic Chemistry.

| Name. | Formula. | Melting Point, Degrees C. | Boiling Point, Degrees C. |
|--|--|---------------------------------|---|
| Benzene. Toluene. m-Xylene (Isoxylene) Ethyl benzene Trimethyl benzenes. (1, 2, 4) = pseudocumene (1, 3, 5) = mesitylene. Isopropyl benzene (Cumene). Cymene. Pentamethyl benzene Hexamethyl benzene Pentaethyl benzene Pentaethyl benzene Hexaethyl benzene Hexaethyl benzene | C ₆ H ₅ · CH ₂ CH ₃ C ₈ H ₃ (CH ₃) ₃ C ₆ H ₅ CH(CH ₃) ₂ C ₆ H ₄ · (CH ₃) ₅ C ₆ H ₄ · (CH ₃) ₅ | 5·4 -54 53 164 129 | 80.4 110.3 139 134 170 164.5 153 175 230 264 277 298 |

Members of the benzene series of hydrocarbons have been isolated from certain petroleums, but it is in the products of destructive distillation that their occurrence is of most interest. They react with sulphuric acid to form sulphones, or sulphonic acids and water. Just as CH₃ or any univalent chain radical may replace a hydrogen atom of the benzene ring, so also may a univalent closed chain radical, and when this occurs compounds having more than one ring nucleus are found. Thus we may have what are known as the polyphenyl hydrocarbons.

Polyphenyls. — The simplest member of this group of hydrocarbons is diphenyl, so called because it is composed of two phenyl radicals joined together. Phenyl (C_6H_5) may be considered as benzene from which one hydrogen atom has been

removed. The formula for diphenyl is, therefore, $C_{12}H_{10}$ or graphically expressed:

As might be expected from a consideration of the other series of compounds, the next member of the diphenyl series is methyl diphenyl or phenyltolyl, having the formula $C_{13}H_{12}$, which differs from diphenyl by CH_2 . The general formula for this series is, therefore, $C_nH_{2^{n-14}}$. Its various members are found most commonly in tars. More complicated compounds containing three, four or more benzene nuclei are known but these need not here be considered.

Naphthalene Series. — The naphthalene series is composed of hydrocarbons having two benzene nuclei condensed to a single nucleus, two carbon atoms being common to both. Somewhat similar examples were noted in the polycyclic polymethylene bridge compounds described above, where three carbon atoms were common to both rings. The first member of the naphthalene series is naphthalene itself, having the formula $C_{10}H_8$, and graphically expressed as follows:

Naphthalene is found principally in coal tar. It is a crystalline compound highly volatile and possessing a peculiar odor. Its presence is probably detrimental in certain classes of road binders and this fact will be discussed in a later chapter. Methyl-naphthalene ($C_{11}H_{10}$) is the next member of this series and occurs in two isomeric modifications, alpha and beta, according to the position of the methyl radical with respect to the carbon atoms common to both benzene rings. The general formula for this series is C_nH_{2n-12} .

Anthracene Series. — In the anthracene series three benzene rings are condensed to a single nucleus and the first member, anthracene $(C_{14}H_{10})$, may be represented as follows:

Like naphthalene anthracene is also a crystalline solid, found principally in tars which have been produced at high temperatures. Methyl anthracene $(C_6H_4:(CH)_2:C_6H_3.CH_3)$ is the next member of the series, whose general formula is C_nH_{2n-18} .

Other Series of Unsaturated Hydrocarbons. — Besides those already mentioned, other series holding an intermediate position between the benzenes and naphthalenes, and naphthalenes and anthracenes, also exist and have been found in bituminous materials. Thus the olefine benzenes, of which styrolene ($C_6H_5CH:CH_2$) is the parent hydrocarbon, have the general formula $C_nH_{2^{n-8}}$. The indene group ($C_nH_{2^{n-10}}$), of which indene (C_9H_8) is the first member, has a condensed nucleus as shown below:

The acenaphthene series (C_nH_{2n-14}) has a still more complicated nucleus, as shown by the graphic formula for its first member acenaphthene $(C_{12}H_{10})$, expressed as follows:

$$\begin{array}{c|c} H_2C & \longrightarrow CH_2 \\ & & \downarrow \\ C & & \downarrow \\ H - C & & \downarrow \\ H - C & & \downarrow \\ C & & \downarrow \\ C & & \downarrow \\ H & & H \end{array}$$

The fluorene group forms still another series, having the general formula C_nH_{2n-16} . Its first member, fluorene, is believed to have the following constitution:

Some members of all of these series are known to exist in coal tar and many have been found in various mineral oils and asphalts. They are almost invariably the products of high temperatures and have been formed by reaction and sometimes by polymerization of certain members of the less complicated open chain series. They are difficult to isolate and indentify and are only mentioned as connecting links between the more important and better known series of hydrocarbons.

Members of another series, which deserve mention, known as the camphan group of terpenes, having the general formula C_nH_{2n-4} , are also found in tars and the bitumens of an asphaltic nature. Camphene is a typical member of this series and may be graphically expressed as follows:

$$\begin{array}{c|c} CH_2 - CH & \longrightarrow CH \\ & CH_3 \cdot \stackrel{|}{C} \cdot CH_3 & \\ CH_2 - C & \longrightarrow CH \\ & CH_3 & \end{array}.$$

Hydrocarbon Derivatives. — As has been noted, oxygen, sulphur and nitrogen derivatives of the hydrocarbons are found in bituminous materials, but usually in far smaller quantities than the hydrocarbons themselves. Their effect upon the physical properties of the bitumens is often of considerable importance. The elements oxygen and sulphur react with many of the hydrocarbons, especially at high temperatures, to form other compounds, and this fact is made use of in the preparation of certain classes of road binders. Somewhat similar reactions have probably been the direct cause of the natural formation of the solid native bitumens.

Oxygen derivatives of the hydrocarbons are known chemically as alcohols, ethers, aldehydes, ketones and acids, and the sulphur and nitrogen compounds are usually considered as direct derivatives of these oxygen compounds. Some of these products will be considered in connection with the individual classes of bitumens in the following chapters. They are so numerous that it is hardly practicable to even classify them in this chapter.

Summary and Conclusions. — While this chapter may to the casual reader appear somewhat involved and irrelevant, it will be found in later portions of this book that the brief description of the hydrocarbons as given above will prove of considerable service in classifying the various forms of bituminous road materials. The more important hydrocarbon series which have been mentioned are summarized in the following table. For more detailed information than that given in this chapter, reference should be made to any of the standard textbooks on organic chemistry.

CLASSIFICATION OF HYDROCARBONS FOUND IN BITUMINOUS ROAD MATERIALS.

| Scries. | General Formula. | Found mainly in | Characteristics. |
|------------------------------|----------------------|--|---|
| Paraffins. | C_nH_{2n+2} | Natural gas. Fastern petroleums | Open chain, saturated. |
| Olefines. | C_nH_{2n} | Ozocerite, Shale oils. Some American | Solids greasy, non-cementitious. Open chain, unsaturated. |
| Naphthenes. | $C_n H_{2n}$ | petroleums, Coal tar. Russian petroleums. American semiasphaltic and | Only. Closed chain, saturated. Intermediate compounds connecting paraffins |
| Acetylenes. | C_nH_{2n-2} | asphaltic petroleums. Coal tars, | with asphaltic hydrocarbons. Open chain, unsaturated. Intermediate compounds connecting paraffins |
| Polycyclic Polymethylenes | CnH2n-6, 4, 6, etc.) | Semiasphaltic and asphaltic petroleums. Asphalt. | with benzenes. Closed chain, saturated and unsaturated. Probably asphaltic. |
| Camphenes. | C_nH_{2n-4} | Tars. Asphaltic bitumens. | Closed chain, unsaturated. Probably impart sticky, resinous properties to substances in which they occur. |
| Benzenes. | C_nH_{2n-6} | Tars. | Closed chain, unsaturated. High temperature products indicative of the presence of bitumens of good binding qualities. |
| Naphthalenes. | C_nH_{2n-12} | Tars, | Closed chain, unsaturated. Crystalline, quite volatile. |
| Anthracenes. | C_nH_{2n-18} | Tars. | Crystalline, waxy. |
| | | | |

CHAPTER VII.

BITUMENS EMPLOYED AS DUST PREVENTIVES AND ROAD BINDERS.

Various types of bitumens employed as dust preventives and road binders have already been mentioned in Chapter II, but before taking up the different classes individually, it may be well to consider their further classification with relation to one another, their origin and methods of formation. bitumen is a generic term that has been made to include a great variety of substances and much confusion has arisen as to just what the word signifies. Any definition which may at the present time be advanced is a purely arbitrary one. A slight modification of Richardson's definition of native bitumens has, however, seemed to the author to convey more nearly a correct idea of the term than any other. According to this definition, bitumens may be described as consisting of a mixture of native or pyrogenetic hydrocarbons and their derivatives, which may be gaseous, liquid, a viscous liquid or solid, but if solid, melting more or less readily upon the application of heat and soluble in chloroform, carbon bisulphide and similar solvents. Mineral organic compounds which are not soluble to any extent in these solvents, but which, upon being subjected to the process of destructive distillation, give rise to the bitumens, are termed pyro-bitumens. Bitumens themselves may be divided into two main classes, native and artificial. The former, as their name implies, occur in nature, while the latter are produced by the destructive distillation of either pyro-bitumens or the bitumens themselves. In certain cases, it is impossible to make a sharp distinction between native bitumens, artificial bitumens and pyro-bitumens, as they often merge into one another. Taken broadly, however, this classification is a most convenient one

to follow when considering the individual types of bituminous materials.

Native Bitumens. — According to Richardson, "Native bitumens consist of a mixture of native hydrocarbons and their derivatives, which may be gaseous, liquid, a viscous liquid or solid, but if solid, melting more or less readily on the application of heat, and soluble in turpentine, chloroform, bisulphide of carbon, similar solvents, and in the malthas or heavy asphaltic oils." Natural gas, petroleum, maltha, ozocerite, hatchettite, fossil resins, numerous varieties of asphalt, glance pitch, manjak, gilsonite and grahamite may all be classed as native bitumens, although some varieties of grahamite closely approach the pyro-bitumens in characteristics. If the liquid native bitumens or petroleums are subjected to the process of distillation or evaporation residues are obtained which can be considered as artificial bitumens only, although in certain respects they may resemble some of the native bitumens. The fact that such a distinction is not clearly understood has been the cause of much confusion among road engineers in regard to the composition of certain asphaltic road oils and residual pitches which have come under their notice. In nature petroleums may be and undoubtedly have been subjected to the process of distillation or evaporation with the production of semisolid and solid bitumens. The character of the original oil as well as the natural conditions attending this transformation have undoubtedly produced the various types of solid native bitumens mentioned above. Thus paraffin petroleums or those composed largely of C_nH_{2n+2} hydrocarbons are the source from which ozocerite and hatchettite have been produced. Cyclic oils containing principally C_nH_{2n} , C_nH_{2n+2} , C_nH_{2n-4} , etc., hydrocarbons both saturated and unsaturated have given rise to the asphalts and other closely related bitumens. The malthas hold an intermediate position between the petroleums and these solid bitumens.

A number of theories have been advanced as to the origin of native bitumens and no one theory has as yet been generally

accepted. In a recent treatise * Peckham states that "generally speaking, the theories advanced fall into three classes, embracing those which regard bitumen as a distillate produced by natural causes, those which regard bitumen as the product of a peculiar decomposition of organic matter within the formations in which the organic matter is enclosed, making the bitumen in a sense indigenous to the rocks in which it is found, and those which regard bitumen as a product of chemical reaction, the latter class being subdivided into those which regard bitumen as a product of chemical change in natural substances of which carbon and hydrogen are constituents, and those which advocate a purely chemical reaction between purely mineral or inorganic materials."

After a somewhat exhaustive review of the available data concerning this subject and the experimental work of many investigators, he strongly advocates the first theory, which is perhaps more satisfactory than any other single theory yet advanced. To quote his summary of the matter: "Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen: hence when these forms accumulated in sediments, which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of the sediments above them, up to the surface. They must also have been distilled under a gradually increasing temperature which would have been largely controlled by the pressure. While the temperature and the pressure would have in every instance been the least possible, with steam always present, these physical conditions would on account of the varying porosity and consequent varying resistance of the overlying mass have produced very great effects in

^{*} Solid Bitumens, page 21. M. C. Clark.

some instances and very slight effects in others. As a consequence, we have in natural bitumens, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

"If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds, from marsh gas to solid paraffin, remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances. The contents of the original reservoirs, borne down and invaded by heat, might become involved in a second distillation at an increased pressure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitrohydrocarbon reaching the surface, under these conditions, might, by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha and become, finally, solid asphaltum, and this, through the lapse of time and abundance of material, on a scale of vast magnitude."

Artificial Bitumens. — The artificial bitumens may be divided into two main classes according to their method of formation, those produced by a partial distillation of the bitumens themselves and those produced by the destructive distillation of the bitumens and pyro-bitumens as well as certain other substances of an organic nature. In the first case two classes of artificial bitumens are formed which are known as distillates and residues. The distillates are almost invariably fluid, while the residues may be fluid, semisolid, or solid according to the extent to which the process of distillation has been carried. If

fluid they are termed residual oils or tars, as the case may be, and if solid should be called residual pitches. Residual pitches which have been produced from asphaltic and semiasphaltic oils are, however, often given the trade name of asphalt, which is very misleading and has caused much confusion among the uninitiated as to what the term asphalt implies. This has led to the use of the expression "asphalt contents" of an oil, by which is meant the residual pitch of a given consistency that may be formed by volatilizing a sufficient quantity of the lighter constituents present. As will be shown later, this term is absolutely erroneous for the reason that such a residue is not, strictly speaking, an asphalt at all and in many cases is not even a measure of the residual contents of the oil, but only of the ability of the oil to produce such residues at high temperatures.

Artificial bitumens produced by destructive distillation are commonly known as tars. The word tar is often compounded with the name of the material which has been subjected to the process of destructive distillation, thus designating its origin, for example, coal-tar, oil-tar, wood-tar. Tars are the liquid distillates obtained by cooling the gases produced by distillation. This distillation being destructive and carried on until little or no more gases are evolved from the material distilled, the residue usually consists of carbon or coke together with any mineral matter which was originally present.

Tars themselves are as a rule distilled or refined before being placed upon the market. Distillation is carried on in a manner quite similar to that employed for oils, and distillates and residues are produced. The distillates are oily liquids which often precipitate crystallizable solids upon cooling. The residues as in the case of oils may be fluid, semisolid or solid. Fluid residues from such distillation are known as refined tars and the semisolid and solid as soft or hard pitches according to their degree of hardness. Distillates and residues from tars are quite different in character from petroleum distillates and residues. They are composed mainly of C_nH_{2n-6} , C_nH_{2n-12} , and C_nH_{2n-18} hydrocarbons and their derivatives.

In all cases, however, the distillates may be said to exhibit little or no binding qualities and can, therefore, never be employed as road binders. They have been used to a slight extent as dust preventives, but are usually unsatisfactory for even this purpose, as they produce a slippery, greasy mud in rainy weather. The residues invariably retain the true binding base of the oil or tar if any was originally present, and when brought to proper consistency, represent that base themselves. If distillation is carried on so that none of the individual constituents of the original oil or tar are chemically altered, a mechanical separation only will be effected and the distillation is said to be a purely fractional operation. Where some of the chemical constituents are broken down into other compounds and chemical reactions are known to take place, due to the high temperature employed, the resulting residue is said to be cracked. In the former case the residue of course more nearly partakes of the nature of the original oil or tar than in the latter. If this cracking is carried beyond a certain point, the residue is apt to be seriously injured for road purposes, and if carried to its ultimate conclusion, results in destructive distillation with the formation of a tar distillate and coke residue.

In order to carry on distillation to the greatest possible extent without cracking, recourse is often had to the use of reduced pressure, and the material distilled under a partial vacuum. By this means the boiling points of all of the constituents are lowered, and many which would under ordinary conditions break down or crack at their normal boiling point, pass over unaltered and are collected in the distillate. Superheated steam is also employed to some extent as a mechanical carrying agent for the heavy oil vapors, which, if not removed, immediately after formation are apt to be cracked by overheating. These methods will be further described under the technical preparation of various types of bituminous road materials.

Pyro-Bitumens. — As has been stated, pyro-bitumens are mineral organic substances which are indifferent to the solvents for the bitumens, but which upon being subjected to destructive

distillation give rise to the formation of artificial bitumens. They are as a class hard substances, which do not melt readily upon the application of heat. According to Richardson, they may be divided into two classes, those derived from petroleum and those derived from direct metamorphoses of vegetable growth. The former are sometimes called asphaltic coals to distinguish them from the coals of direct vegetable origin. The minerals albertite nigrite, wurtzelite and certain varieties of grahamite constitute the asphaltic coals, while peat, lignite. bituminous and semibituminous coals, and bituminous shales and schists compose the latter class. Certain of these materials yield, upon destructive distillation, distillates quite similar to some of the native bitumens. The majority, however, yield tars which are quite unlike any of the native bitumens. The manner in which the distillation is carried on as well as the temperatures employed of course govern to a great extent the nature of the artificial bitumen produced.

Classification of Bituminous Materials. — In the following tabular arrangement of bituminous materials, Richardson's classification of the native bitumens and pyro-bitumens has been closely followed by the author, as representing the views of one of the highest authorities on the subject. The artificial bitumens have been classified in such a way as to separate the road binding materials from those which have no road binding qualities, and in both the native and artificial bitumens those of most importance from the standpoint of road treatment and road construction have been printed in capitals.

BITUMINOUS MATERIALS.

I. NATIVE BITUMENS.

(a). Gases.

- 1. Marsh gas. Formed by the decomposition of vegetable matter under water.
- 2. Natural gas. Formed under similar conditions to petroleum and often accompanying it.

(b). Petroleums.

- I. Paraffin oils. Consisting principally of C_nH_{2n+2} hydrocarbons and rich in solid paraffins. Of little value as dust preventives and having practically no binding value.
- 2. Cyclic Oils (Asphaltic). Consisting principally of polymethylene hydrocarbons of the series C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , etc., together with a certain amount of unsaturated hydrocarbons and their derivatives; excellent dust preventives and possessing, or capable of developing under service conditions, considerable binding value.
- 3. Semiasphaltic Oils. Consisting mainly of a mixture of paraffin hydrocarbons and stable polymethylenes; holding an intermediate position between the paraffin and asphaltic oils; good dust preventives, but rather poor road binders unless properly refined.

(c). MALTHAS.

Transition products between petroleum and asphalt, originating from polymethylene oils; often found impregnating porous sandstones and limestones, the individual particles of which are thus bound together, forming in many cases excellent road surfacing materials.

(d). Solids. (Commonly classified as minerals.)

- 1. Paraffin substances such as **ozocerite**, hatchettite, etc. Resembling paraffin wax and having no commercial importance as road binders.
- 2. Amber and fossil resins. Consisting largely of unsaturated cyclic hydrocarbons such as the terpenes.
- 3. ASPHALTIC SUBSTANCES. Originating in polymethylene petroleums, the more volatile hydrocarbons and probably many of the less volatile consisting of complex unsaturated compounds; many of them excellent road binders when cut with a suitable fluxing agent, but of

no value for this purpose when in their natural condition owing to their brittleness; among the most important members may be mentioned the following types which at the present time have not been satisfactorily defined as to differences in composition and physical properties: asphalts (such as Trinidad, Bermudez, California, Cuba, etc.), glance pitch, Manjak, Gilsonite, Grahamite.

II. PYRO-BITUMENS.

- (a). Derived from petroleum (asphaltic coals).
 - 1. Albertite.
 - 2. Wurtzilite.
- (b). Derived from direct metamorphosis of vegetable matter.
 - 1. Peat.
 - 2. Lignite.
 - 3. BITUMINOUS COAL. Source of coal tar.
 - 4. Semi-bituminous coal. Approaching anthracite, which is not strictly speaking a pyro-bitumen.
- (c). Bituminous schists and shales.

III. ARTIFICIAL BITUMENS.

- (a). Derived from the destructive distillation of bitumens and pyro-bitumens, mainly petroleum and bituminous coal, and known as tars.
 - I. Oil tars. Water Gas Tars. Thin oily liquids mixed with considerable quantities of water; consisting principally of unsaturated cyclic hydrocarbons of the C_nH_{2n-6} , C_nH_{2n-12} and C_nH_{2n-18} series together with saturated compounds; serviceable as dust preventives but of little or no value as road binders in their natural state.
 - 2. Coal Tars. Viscous sticky liquids mixed with a certain amount of water; consisting mainly of C_nH_{2n-6} , C_nH_{2n-12} and C_nH_{2n-18} hydrocarbons with their oxygen derivatives known as phenols, cresols, etc., together with sul-

phur and nitrogen derivatives; often excellent dust preventives but unsatisfactory as road binders in their crude state.

- (b). Derived from the fractional distillation of petroleum.
 - I. Distillates. Chemically identical with portions of the original oil unless cracking has occurred during distillation; having no binding value and being unsuitable for use as dust preventives. Among this class of materials may be mentioned petrolic ether, benzine, kerosene or illuminating oil, and some lubricating oils.
 - 2. Residues. Varying in nature according to the character of the original oil and the extent to which distillation has been carried, but composed mainly of unaltered portions of the original oil unless cracking has been resorted to.
 - (aa). Reduced oils.

Fluid products from which only the most volatile portions have been removed; but little used in the treatment of roads.

(bb). RESIDUAL OILS.

Viscous products resulting from the removal of all volatiles to and including the lubricating oils; of little value as dust preventives and of no value as road binders if derived from paraffin petroleums; if produced from semiasphaltic or asphaltic oils their value for road purposes is proportional to their asphaltic characteristics and consistency. Often valuable fluxing agents for solid bitumens too brittle to be used in their original condition.

(cc). Residual Pitches. Semisolid and solid products sometimes called artificial or oil asphalts. The softer varieties give excellent results as road binders if of asphaltic oil origin. Sometimes these products are blown with air while hot, which produces a cheesy non-ductile residue of inferior

road building qualities if the blowing process is carried too far. In order to make the harder residual pitches suitable for road work, it is necessary to cut them with a fluxing oil as in the case of native asphalts.

- (c). Derived from the fractional distillation of tars.
 - I. Distillates chemically identical with portions of the original tar. Of no importance as dust preventives and of no value as binders. Among the distillates may be mentioned water, light oils, carbolic oils, creosote oils and anthracene oils. Solid substances such as naphthalene and anthracene crystallize out of some of these distillates. The creosote and anthracene oils while possessing no binding value themselves serve as excellent fluxing mediums for the hard pitches which exhibit a true binding value.
 - 2. Residues. Varying in nature according to the character of the original tar and the extent to which distillation has been carried; composed mainly of the unaltered heavier products of the original tar.

(aa). DEHYDRATED TARS.

Fluid products from which only the water has been removed. If derived from oil they show little road binding characteristics, but are good dust preventives; if from coal they are often of considerable value both as dust preventives and semipermanent binders.

(bb). REFINED TARS.

Viscous products holding an intermediate position between the dehydrated tars and the pitches. If properly prepared either from water gas or coal tar they are of considerable value as road binders. If, however, they contain large quantities of crystallizable solids and free carbon their value for road purposes is greatly lessened.

(cc). PITCHES.

Semisolid and solid residues, the softer varieties being adapted for use as binders in road construction. The harder pitches are too brittle for road purposes and have to be fluxed with lighter tar products before they can be so used.

Summary and Conclusions.— In this chapter bituminous materials, including native bitumens, pyro-bitumens and artificial bitumens, have been described and classified with special reference to the subject of this book. It is realized that the classification is not complete, inasmuch as the artificial bitumens obtainable from such pyro-bitumens as peat, lignite, bituminous shales, etc., and from wood, bone and other organic substances, have not been included. As such materials, however, are of very slight importance so far as dust preventives and road binders are concerned, it has been thought unnecessary to consider them in this classification.



CHAPTER VIII.

PETROLEUM AND PETROLEUM PRODUCTS.

Petroleums, rock oils or mineral oils are fluid native bitumens widely distributed over the earth, the largest quantities being found in the United States and Russia. Petroleums differ widely in characteristics according to the locality from which they are derived, and while those occurring in the United States will be mainly considered in this chapter, it should be understood that remarks relative to their value as dust preventives and road binders are also applicable to oils from many other countries, as nearly all of the important types are here represented.

The petroleum industry in this country starting with the production of about two thousand barrels in 1859, valued at \$32,000, has in the period of fifty years assumed enormous proportions, the total output for 1908 alone being nearly 180,000,000 barrels or 7,560,000,000 gallons, with a total value of nearly \$130,000,000. This represents about 63 per cent of the world's total output for 1908.

According to Day,* "In all nearly two billion barrels have been produced in forty-nine years, worth one and three-fourths billion dollars. This is more than half the value of all our gold and more than the entire value of our silver produced in twice as many years. The value of the petroleum in 1908 exceeded the value of the gold and silver combined by over two million dollars." The following table gives the total quantity and value of crude petroleum produced in the United States and the average price per barrel of forty-two gallons in 1907 and 1908 by states.

^{* &}quot;The Production of Petroleum in 1908." "Mineral Resources of the United States, Calendar Year 1908." U. S. Geological Survey.

| | | 1907. | | | 1908. | |
|-----------------------|-------------|---------------------------|---------------------------------|-------------|---------------------------|---------------------------------|
| State. | Quantity. | Value. | Average price per Barrel. | Quantity. | Value. | Average price per Barrel. |
| | Barrels. | 6 | 6 | Barrels. | | 9 |
| Colorado | 39,748,375 | \$14,099,950 272.813 | \$0.370 .822 | 44,054,737 | 346,403 | .013 |
| Illinois | 24,281,973 | 16,432,947 | .677 | 33,685,106 | 22,648,88I | .672 |
| Indiana | 5,128,037 | 4,536,930 | .885 | 3,283,629 | 3,203,883 | 976. |
| Kentucky | 820.844 | 862,206 | 104. | 727,767 | 706.811 | 140. |
| Tennessee* Louisiana. | 5,000,221 | 4,063,033 | .813 | 6,835,130 | 4,131,173 | .604 |
| Michigan | 4,000 | 6,500 | 1.625 | 15,246 | 22,345 | 1.466 |
| New York | 1,212,300 | 2,127,748 | 1.755 | 1,160,128 | 2,071,533 | 1.7856 |
| Oklahoma | 12,207,440 | 14,709,880 | 1.210 | 10,050,797 | 14,176,502 | .386 |
| Pennsylvania | 9,666,6 | 17,579,706 | 1.758 | 9,424,325 | 16,881,194 | 1.7912 |
| Texas. | 12,322,696 | 10,401,863 | .844 | 11,206,464 | 6,700,708 | .598 |
| Utah Wyoming | 9,339 | 21,883 | 2.343 | 17,775 | 27,920 | 1.57 |
| West Virginia | 9,005,296 | 15,852,428 | 1.743 | 9,523,176 | 16,911,865 | 1.776 |
| • | 166,095,335 | 166,095,335 \$120,106,749 | \$0.723 | 179,572,479 | 179,572,479 \$129,706,258 | \$0.722 |
| | - | | | | | |

* No production in Tennessee recorded in 1908.

According to physical and chemical properties as well as to geological formation, the petroleums of the United States may be classified under a number of fields. The location from which an oil is obtained may, therefore, be considered an index of its general character, and so of its value as a dust preventive or road binder. The custom of grouping oils according to the quality has become quite general in the trade. A number of terms, such as "Pennsylvania grade," "Lima grade" and "Kansas grade," are in common use, the distinction being based both on the percentage of sulphur and on the proportion of artificial asphalt and paraffin wax to the illuminating oil obtainable from the crude.

The value of an oil as a permanent dust preventive and road binder lies in the quality and quantity of high binding bituminous base retained by the road surface after evaporation of the more volatile constituents. The bases present in petroleums vary from the almost pure paraffin to the almost pure asphalt, many being a mixture of the two. While the paraffin oils are of much more value than the asphaltic from a commercial point of view, the opposite is true from the standpoint of dust suppression. A wholly paraffin oil is of value only as a temporary binder or dust layer, while an asphaltic oil, owing to the character of the base contained, ranks very favorably with other materials as a permanent binder. Petroleum is a mixture of a great number of hydrocarbons together with comparatively small quantities of sulphuretted, nitrogenized, and oxygenated compounds. The approximate composition of crude petroleum is ordinarily determined by distillation, but a knowledge of the residuums left after distillation is of far more value from the standpoint of road treatment. Considerable attention has been paid to these residuums, as well as to the characteristics shown by oils from the various fields.

Oil Fields in the United States. — There are six distinct oil fields in the United States, known as (1) the Appalachian Field, (2) the Lima-Indiana or Ohio-Indiana Field, (3) the Illinois Field (recently classified as such), (4) the Mid-Continent Field,

(5) the Gulf Field and (6) the California Field. Small quantities of oil have also been found in Wyoming, Colorado, Missouri, Michigan and Utah and occur in Arkansas, Montana, Washington, Oregon, Idaho and Nevada. The following table* gives the production of crude petroleum in barrels, in the United States for the years 1903 to 1908, inclusive, by fields.

| Field. | - 1903. | 1904. | 1905. |
|--|--|---|---|
| Appalachian | 31,558,248 24,080,264 | 31,408,567 24,689,184 | 29,366,960 22,294,171 181,084 12,535,777 36,526,323 33,427,473 385,792 |
| | 100,461,337 | 117,080,960 | 134,717,580 |
| Field. | 1906. | 1907. | 1908. |
| Appalachian Lima-Indiana Illinois. Mid-Continent Gulf California Other | 27,741,472 17,554,661 4,397,050 22,838,553 20,527,520 33,098,598 336,082 | 25,342,137 13,121,094 24,281,973 46,846,267 16,410,299 39,748,375 345,190 | 24,945,517 10,032,305 33,685,106 48,323,810 17,318,330 44,854,737 412,674 |
| | 126,493,936 | 166,095,335 | 177,572,479 |

Appalachian Field. — The Appalachian field extends from western New York in a general southwesterly direction along the western side of the Allegheny Mountains, through Pennsylvania, eastern Ohio, the northwestern part of West Virginia into eastern Kentucky and Tennessee. In parts of Ohio, Kentucky and Tennessee, the oils vary in character and some closely resemble the products of the Lima-Indiana field. The oils of the Appalachian field as a class are practically free from sulphur and asphaltic hydrocarbons, but rich in paraffins, both liquid and solid. They are the most valuable of all crude oils as they

^{*} Report of Geological Survey, loc. cit.

yield the largest percentage of gasoline and illuminating oils. During the year 1908, this field produced about 14 per cent of the total output of oil in the United States, the crude material selling for about \$1.76 per barrel. The Pennsylvania oils in particular have been closely studied by Mayberry, Young, Richardson and others as being representative examples of the Appalachian field. According to Richardson, "The paraffin petroleums of the Appalachian field consist of small amounts of monocyclic aromatic and polymethylene hydrocarbons, which have been separated in such a degree of purity as to be identified definitely; of minute traces of sulphur and nitrogen compounds and predominatingly, of paraffin hydrocarbons from isobutane (C₄H₁₀) to C₃₅H₇₂, the members above 14 being solids at ordinary temperatures. Polycyclic hydrocarbons of the C_nH_{2n} series are also present in very considerable amounts, from C21 to C28, the constitution of which is not understood but which are quite different from the hydrocarbons of the same relation of carbon and hydrogen found in asphaltic oils, and have no relation to the ethylene or olefine series. Polycyclic hydrocarbons of the C_nH_{2n-2} series are also present in the fractions boiling above 200° at 50 mm. The two latter classes of hydrocarbons are worthy of careful study. They are saturated, in that they are not acted upon by strong sulphuric acid, and are all sharply differentiated from the hydrocarbons of the asphaltic petroleums of California by their physical properties."

The characteristics of dense residuums obtained from these oils are represented by the following results obtained from an examination of a Pennsylvania oil residuum by Richardson, who has made a particular study of residuums as of interest in the paving industry

(a) PENNSYLVANIA OIL RESIDUUM.* PHYSICAL PROPERTIES.

| Specific gravity, | 25°/25° | C | | | 0.9202 |
|-------------------|---------|---|------|------|--------|
| Flash, degrees C | D | | | | 186° |

^{*} This and other analyses marked (a) are taken from VI Congresso Internazionale di chimica applicata, Roma, 1906. Communicazione fatta nella Sezione IV.—A. (Industrie dei prodotti organici).

CHEMICAL CHARACTERISTICS.

| Loss at 160°, 7 hours. Character of residue. Loss at 205°, 7 hours (fresh sample). Character of residue. | 5·3% Soft. 14·2% Soft. |
|---|---------------------------------|
| Character of residue to constant weightBrittl | |
| Bitumen soluble in CS ₂ , air temperature | 99.8% |
| Organic matter, insoluble | 0.2% |
| Inorganic or mineral matter | 0.0% |
| | 100.0 |
| Bitumen insoluble in 88°B, naphtha, air temperature | 4.3% |
| Per cent of soluble bitumen removed by H ₂ SO ₄ | 21.9% |
| Per cent of total bitumen as saturated hydrocarbons | 74.8% |
| Per cent of solid paraffin | 11.0% |
| Fixed carbons. | 3.0% |

The brittle pitch noted above is probably formed by molecular condensation at high temperatures, which will be discussed later in this chapter, and was not present in the original oil. It will be noted that this residue contains a much higher percentage of solid paraffin than the oil residues from any but the Lima-Indiana oils. Such oils are unsuited for road purposes either in their crude or refined state, except as fluxes for certain solid bitumens of an asphaltic nature.

Lima-Indiana Field. — This field includes the northwestern part of Ohio and middle Indiana. At one time the Illinois field was included, but it has since been shown to constitute a field by itself. The Lima-Indiana oils, although classed as paraffin petroleums, are denser than those obtained from the Appalachian field, and contain much larger quantities of sulphur compounds, which give them a disagreeable odor and make a special treatment necessary while being refined. They produce less illuminating oils than the Appalachian petroleums and are, therefore, less valuable, the price per barrel during 1908 being about one dollar. The output for that year amounted to about 5.6 per cent of the total oils produced in the United States.

Considerable quantities of solid paraffins are found in the Lima-Indiana field, and certain asphaltic hydrocarbons which are not present in the Appalachian oils. Saturated C_nH_{2n} and C_nH_{2n-2} hydrocarbons of higher boiling point begin at a much

lower number of carbon atoms than in the Appalachian oils, and hydrocarbons of the series C_nH_{2n-4} are found which do not exist in the latter. Larger amounts of naphthenes and unsaturated hydrocarbons are also found. The characteristics of a typical dense Ohio oil residuum are shown in the following table:

(a) OHIO OIL RESIDUUM. PHYSICAL PROPERTIES.

| Specific gravity, 25°/25° C. Flash, degrees C. | 0.9318 224° |
|---|----------------|
| CHEMICAL CHARACTERISTICS. | |
| Loss, 160° C., 7 hours | 0.3% |
| Character of residue | Soft. |
| Loss, 200° C., 7 hours (fresh sample) | 7·4% Soft. |
| Bitumen soluble in CS ₂ , air temperature | 99.4% |
| Organic matter, insoluble | 0.6% |
| Inorganic or mineral matter | 0.0% |
| | 100.0 |
| Bitumen insoluble in 88° B. naphtha, air temperature | 3.8% |
| Per cent of soluble bitumen removed by H ₂ SO ₄ | 17.0% |
| Per cent of total bitumen as saturated hydrocarbons | 83.0% |
| Per cent of solid paraffin | 11.4% |
| Fixed carbon | 3.7% |

It will be seen that this residuum is quite similar to that obtained from the Pennsylvania oil. Such products are, therefore, of no value as road binders.

Illinois Field. — The Illinois field, being of more recent development, has not received as much study as the two preceding fields. In general the Illinois oils contain less sulphur than the Lima-Indiana oils, although they vary within wide limits. Some contain considerable quantities of asphaltic hydrocarbons and approach in character oils found in the Gulf field. This is also true of certain Kentucky oils which seem to be closely related to those found in southern Illinois. Both these Illinois and Kentucky oils have been used to a considerable extent in the treatment of roads. The value of Illinois oils during 1908 was considerably less than the Lima-Indiana oils, being sold at about sixty-seven cents per barrel, a difference of thirty-three cents. The output for this field in 1908 was very large, represent-

ing about 18.8 per cent of the total output of the United States. An examination of a southern Illinois oil residuum, made by the author, showed it to possess the following characteristics:

ILLINOIS OIL RESIDUUM. PHYSICAL PROPERTIES.

| Character Viscous, slightly | y sticky. |
|--|-----------|
| Specific gravity, 25°/25° C | .941 |
| Flash, degrees C | 187° |
| CHEMICAL CHARACTERISTICS. | |
| Loss 163°, 5 hours | 1.46% |
| Character of residue | Soft. |
| Bitumen soluble in CS ₂ , air temperature | 99.8% |
| Bitumen insoluble in 86° naphtha, air temperature | 5.9% |
| Fixed carbon | 4.0% |

Mid-Continent Field. — This field embraces southeastern Kansas, the eastern part of Oklahoma and northern Texas. Like the Illinois field, it produces oils of very varied character, but as a rule denser than the eastern oils. Solid paraffins are present but also considerable quantities of the C_nH_{2n} , C_nH_{2n-2} and C_nH_{2n-4} hydrocarbons. They may be said to contain a semiasphaltic base and for road treatment rank with the southern Illinois and Kentucky oils in value. In 1908 the Kansas field produced more oil than any of the others, the output being 26.9 per cent of the total output of the United States. These oils were lower in price than any of the others, being about thirty-nine cents per barrel. The characteristics of a Kansas oil residuum are shown in the following table:

(a) KANSAS OIL RESIDUUM. PHYSICAL PROPERTIES.

| Specific gravity, 25°/25° C | 0.9328 196° |
|---|----------------|
| CHEMICAL CHARACTERISTICS. | |
| Loss, 100° C., 7 hours | 2.6% |
| Character of residue | Soft. |
| Loss, 200° C., 7 hours (fresh sample) | 5.7% |
| Character of residue | Soft. |
| Bitumen insoluble in 88° naphtha, air temperature | 3.6% |
| Per cent of soluble bitumen removed by H ₂ SO ₄ | 14.4% |
| Per cent of solid paraffins | 7.8% |
| Fixed carbon | 4.1% |

Gulf Field. — Louisiana and all of Texas but the northern portion are included in this field. The Gulf oils contain a much smaller percentage of solid paraffins than any of the others so far mentioned, and a greater percentage of unsaturated hydrocarbons. They are as a class more asphaltic in character and, therefore, more suitable for use as road binders. Many of them have a high sulphur content and evolve a considerable amount of hydrogen sulphide. They are more stable than the truly asphaltic oils and in this respect are superior. Their binding value is, however, less. They are well suited for fuel oils and yield valuable lubricating oils. In 1908 the Gulf field produced about 9.6 per cent of the total oil output of the United States, and sold at an average price of a little less than sixty cents per barrel.

The characteristics of a typical dense Gulf oil residuum, obtained from the Beaumont district, are shown in the following table:

(a) GULF OIL RESIDUUM. PHYSICAL PROPERTIES.

| Specific gravity 25°/25° C | 0.9735 |
|---|---------------|
| Flash, degrees C | 214° |
| | |
| CHEMICAL CHARACTERISTICS. | |
| Loss, 160°, 7 hours | $\circ.8\%$ |
| Character of residue | Soft. |
| Loss, 200°, 7 hours (fresh sample) | 6.2% |
| Character of residue | Soft. |
| Bitumen soluble in CS ₂ , air temperature | 99.6% |
| Organic matter insoluble | 0.4% |
| Inorganic matter | 0.0 |
| | 100.0 |
| Bitumen insoluble in 88° naphtha, air temperature | 4.8% |
| Per cent of soluble bitumen removed by H ₂ SO ₄ | 20.9% |
| Per cent of total bitumen as saturated hydrocarbons | 79.4% |
| Per cent of solid paraffins | 1.7% |
| Fixed carbon | $3 \cdot 5\%$ |
| | |

California Field. — While the petroleums of California consist mainly of asphaltic hydrocarbons, their density varies within such wide limits that they should properly speaking be divided into two classes, light grade and heavy grade oils. While paraffin petroleums do occur to some extent, in the

majority of oils from this field, the solid paraffins are never found. Hydrocarbons of the C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , C_nH_{2n-8} have been found, as have also phenols and other aromatic hydrocarbons. Nitrogeneous bodies often occur to a large extent and sulphur compounds are also present. The principal characteristic of California petroleums, as differentiating them from those of the other fields, is that their residues consist largely of unstable polycyclic polymethylenes and thus closely resemble the native asphalts in character. Advantage has been taken of this fact for the purpose of manufacturing artificial asphalts, which are often hard to distinguish from some of the natural products. For use as road binders, the California oils are undoubtedly superior to all others.

In 1908, the California field produced about 25 per cent of the total output of the United states, and sold at an average price of fifty-two cents per barrel, which is lower than that of any of the other oils, except those of the Mid-Continent field.

The characteristics of a typical California oil residuum are shown below:

(a) CALIFORNIA OIL RESIDUUM.

| PHYSICAL PROPERTIES. | |
|---|-------|
| Specific gravity, 25°/25° C | 1.006 |
| Flash, degrees C | 1910 |
| CHEMICAL CHARACTERISTICS. | |
| Loss, 160° C., 7 hours | 3.2% |
| Character of residue | Soft. |
| Loss, 200° C., 7 hours (fresh sample) | 17.3% |
| Character of residue | Soft. |
| Bitumen soluble in CS ₂ , air temperature | 99.7% |
| Organic matter insoluble | 0.3% |
| Inorganic matter | 0.0% |
| | 100.0 |
| Bitumen insoluble in 88° naphtha, air temperature | 7.7% |
| Per cent of soluble bitumen removed by H ₂ SO ₄ | 54.9% |
| Per cent of total bitumen as saturated hydrocarbons | 41.9% |
| Per cent of solid paraffin | 0.0% |
| Fixed carbon | 6.0% |

Other Fields. — Oils from the other fields have not been as closely studied as the preceding, but a few observations may be made as to their characteristics. In general the Wyoming oils

vary from semiasphaltic to the almost wholly asphaltic, while the Colorado oils seem to be rich in paraffins and are in many respects similar to the eastern petroleums. To the author's knowledge, neither of these oils has been employed to any extent as a dust preventive or road binder. Oils from other individual fields resemble either the Pennsylvania, Texas or California oils, which may be considered as representing the three main types.

Owing to the extremely complex nature of petroleums and the fact that one type blends into another, only the very broadest distinction can be made between the different types, and the preceding description of characteristics of oils from the various fields should be considered in this light, as no one oil will exactly duplicate another even in the same field.

Occurrence of Petroleum. — Petroleum is not limited to any particular geological horizon, but is found in rocks of all ages from the lower Silurian to the most recent. It is generally found in sandstones or conglomerates overlaid with an impervious shale or slate. In many places it comes to the surface in small quantities but is generally obtained by boring tube wells through the shale into the sand rock. After the deposit or well has been struck, the pressure is sometimes so great as to drive the oil to the surface with much force. Such wells are called gushers, but seldom flow for more than a few days without pumping becoming necessary. In many cases the well is torpedoed in order to bring the oil to the surface. This is done by exploding a shell, containing nitroglycerin, which has been lowered to the bottom of the well, the resulting pressure being sufficient to force the oil out of the boring for some time. The wells vary in depth from 50 to 4000 feet and over, and the oil is now generally carried from these wells to the refineries by pipe lines through which it is pumped from station to station. When the crude oil is extremely viscous, recourse is had to a pipe rifled in much the same manner as a gun barrel. A small quantity of water is pumped with the oil, and this, owing to the centrifugal motion caused by the rifling, finds its

way to the inner surface of the pipe and serves as a lubricant between it and the oil.

Crude petroleum is an oily liquid of rather unpleasant odor with a specific gravity ranging from 0.73 to 0.98 and higher according to the locality from which it is derived. It varies in color from greenish brown to nearly black and often exhibits a reddish brown or orange color when viewed by transmitted light. It is also somewhat fluorescent. Sand and water are often mixed with the crude oil but these separate and settle upon standing in the storage tanks. Crude petroleum has been used to some extent, especially in California, for direct application as a dust preventive. It has also been employed in considerable quantities as a fuel and in some instances has been used as a lubricant without previous treatment. In order to recover various products from the crude petroleum it is subjected to a process of refining by means of fractional distillation. In general the process is carried on as follows, with the production of five fractions, the naphthas, the illuminating oils, the lubricating oils, paraffins and the residue which if distillation is carried to a finish becomes coke. The higher the yield of illuminating oils the greater the value of the crude material. Many crude products are, however, distilled for lubricating oils only. The process of refining is for the most part worked in two stages, the light oils being removed in the first and the heavier oils in the second.

Oil Stills. — There are two forms of stills used for distilling the light oils, the cylindrical and the cheese box. The former is most commonly employed in this country. It is constructed of iron and is set in a horizontal position in a brick furnace with the upper half exposed to the air as shown in Fig. 14. It is fitted with steam coils for quickly heating the whole mass of oil, and sometimes with an arrangement for blowing in free steam which assists mechanically in carrying over the oil vapors through the dome and exit pipe to the condensers. The cheese box still is set directly over the furnace and all except the bottom is exposed to the outside air. It is also fitted with steam coils

and jets and the bottom is double curved to admit of expansion. It is not now very generally employed. The condensers consist either of coils of iron pipe or batteries of parallel pipes cooled

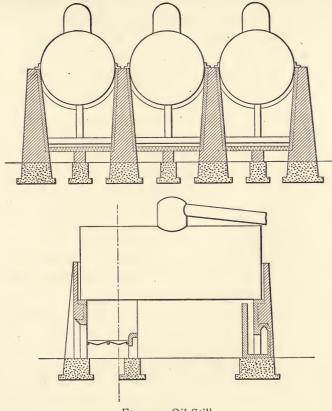


Fig. 14. Oil Still.

with water. They are usually provided with traps by means of which the gases passing over with the oils are collected and led under the still to be burned.

Preliminary Refining. — In carrying on this operation, the oil, which has been allowed to settle in the storage tank until the mud and water have settled out, is charged into the still and heated by means of the furnace and the steam coils until the first fraction, or naphthas, begins to flow from the condenser.

When the fractions boiling as high as 150° C. have appeared, the distillate has a specific gravity of about .729 and the oils thus collected are reserved for further fractionation and purification. The oils from 150° to 300° C., having a specific gravity of from .700 to .820, next appear and are collected for further purification, after which they are employed for illuminating purposes. These are known as kerosenes or burning oils, and as they are the most valuable of any of the constituents, a method known as "cracking," which increases their yield, is very generally employed. As soon as the heavy oils begin to appear the fire is modified so that only the bottom of the still is heated very hot, while the top and sides, being exposed to the air, become somewhat cooled. The heavy oil vapors are therefore condensed within the still itself and upon dropping back into the residuum, which is much hotter than their boiling points, break up into lighter oils with lower boiling points and often with a separation at the same time of free carbon or coke, which is deposited upon the bottom of the still.

Further Refining. — The residuums, or reduced oils, produced by the method of distillation which has been described, are often further treated to remove the burning oils and paraffins. For this purpose they are transferred to a cylindrical still set in much the same way as the one for removing the lighter oils. This still is called the tar still and is usually smaller than the one previously mentioned. It is fitted with pipes for introducing superheated steam. The distillate up to 400° C. constitutes the lubricating oils. These often contain a considerable amount of paraffin scale, which is separated by further treatment. The oils containing solid paraffins are the last to appear and if distillation is carried far enough the residue becomes coke. If distillation is not carried to this point and the petroleum is a paraffin one, the residue remaining after the greater part of the oils have been removed is treated to recover vaseline as well as paraffin. Sometimes distillation is carried on in vacuo, by which means the heavier distillates are removed at a lower temperature than otherwise and cracking is avoided

to a considerable extent. This is desirable if a large yield of solid paraffins is to be obtained or an artificial asphalt is to be produced.

Some residues are employed as fuel, having little value for any other purpose, some which should be used as a fuel are sold as road preparations and their use for road treatment has resulted in many failures. If distillation is carried to the point where a solid residuum is obtained upon cooling, an artificial asphalt is produced, providing the crude oil is asphaltic in character. The artificial asphalts have been extensively employed in recent years in the paving industry and are now being sold to some extent as road binders.

Cracking. — The chemistry of the cracking process is exceedingly complex and but little understood. Under the varying conditions at which it takes place, including pressure, temperature and character of the oil distilled, reactions involving any or all of the hydrocarbon series may occur accompanied by the splitting up and polymerization of certain compounds. At such times the gaseous components present in the still are in an extremely unstable state of equilibrium and are ready to break up or react with one another in different ways to form varying products, according to slight variations in temperature and pressure. It is certain, however, that the general tendency of these reactions is towards the formation of unsaturated compounds as shown by the behavior of the distillates with sulphuric acid. Thus the hydrocarbon C20H42 might be resolved into $C_5H_{12} + C_{15}H_{30}$, or $C_6H_{14} + C_{14}H_{28}$, etc., the general equation of the decomposition being:

$$C_nH_{2n+2}+$$
 heat $=C_{(n-p)}H_{2(n-p)+2}+C_pH_{2p}$ paraffin Olefine

According to Thorpe and Young * the product actually obtained is a mixture of several paraffins and several olefines.

If the cracking process is not carried too far, certain hydrocarbons of asphaltic characteristics may be formed, but if it is

^{*} Ber. des Deutsch. Chem. Gesellsch., 1872, p. 536.

carried beyond this point inert coke or free carbon is deposited in the residuum. The presence of this substance in any quantity is direct evidence that the oil has been cracked. There is a much greater tendency for asphaltic oils to crack at comparatively low temperatures than the paraffin oils and for this reason where it is desired to produce a residuum suitable for road or paving work, great care should be taken in distilling for, even if the stills are subjected to a uniform temperature, cracking begins to take place at ordinary pressures before residuums of sufficient consistency can be secured, and for this reason the vacuum process with or without the use of superheated steam is largely employed. By this means residues are produced which more nearly resemble the semisolid and solid native bitumens than if the distillation were conducted under normal conditions. It should be remembered, however, that the native bitumens have been formed under conditions which it has so far been impossible to reproduce either in the laboratory or factory, and the exact duplication of native products has, therefore, been an impossibility. While the asphaltic oils if carefully distilled or evaporated may be converted into artificial asphalts, closely resembling the native, this can be only partially accomplished with the semiasphaltic oils and not at all with paraffin petroleums. For this reason the California oils are far superior to those from other fields, for the purpose of manufacturing artificial asphalts. In general it may be said that as asphalts are produced from certain oils in nature by evaporation, decomposition and polymerization of certain classes of hydrocarbons so also are the artificial asphalts by similar artificial processes, but the temperatures required to bring about these results in the latter case are probably greater than in the former, owing to the necessarily rapid conversion and lower pressure.

Blown Oils and Similar Products.— In nature oxidation or dehydrogenezation undoubtedly plays an important part in the formation of asphalts and this is caused by the action of some strong oxidizing agent such as oxygen or sulphur. These sub-

stances may react with two similar hydrocarbon molecules to form a single hydrocarbon together with water or hydrogen sulphide gas (H_2S) . When such reactions occur between ring compounds a nucleus condensation often results. The formation of the polycyclic polymethylenes is thus explained. This method of nucleus condensation may be represented by the following general reactions:

(1)
$${}_a\mathrm{C}_n\mathrm{H}_{2n}+{}_b\mathrm{S}=\mathrm{C}_{an}\mathrm{H}_{2an-2b}+{}_b\mathrm{H}_2\mathrm{S}$$

Polymethylene + Sulphur =Polycyclic Polymethylene + Hydrogen Sulphide.

(2)
$${}_a\mathrm{C}_n\mathrm{H}_{2n} + {}_b\mathrm{O} = \mathrm{C}_{an}\mathrm{H}_{2an-2b} + {}_b\mathrm{H}_2\mathrm{O}$$

Polymethylene + Oxygen. = Polycyclic Polymethylene + Water.

Other reactions in which the elements actually combine with the hydrocarbons to form sulphuretted or oxygenated compounds may also occur. Attempts have been made to reproduce these reactions in the still by artificial means. The first artificial asphalt made in this manner was produced by the action of sulphur, which was added to an ordinary paraffin petroleum residuum while hot after the distillation had been stopped. Hydrogen sulphide gas was evolved and the residuum was thickened considerably, but became very cheesy. This method was known as the Dubbs process and was succeeded by that of Byerly, who found that much the same results could be produced by blowing a jet of air through the hot residue in practically the same way that certain vegetable oils are treated in order to thicken them. Products of this nature are now manufactured to a large extent, and are generally known as blown oils. The paraffin hydrocarbons are little acted upon by oxygen, even at comparatively high temperature, so that the thickening of paraffin petroleums by this means is largely dependent upon the reactions taking place between the oxygen and hydrocarbons of other series. Unless considerable quantities of asphaltic hydrocarbons are present, in which case the oil would be semiasphaltic, blown oils are of no value as road binders. The semiasphaltic blown oils are now used to a considerable extent in the treatment of roads and promise to be of

value if the blowing process has not been carried too far and if only a comparatively small percentage of heavy paraffin hydrocarbons is present. They exhibit fairly good binding qualities and have the advantage of being less susceptible to temperature changes than almost any other type of bitumen. Their main drawback seems to lie in the fact that they are not ductile, but in the case of soft and medium hard products this is not an exceedingly serious objection. They have a tendency to harden with age, but so also have the truly asphaltic oils and this should be remembered when selecting a road binder, in order that too brittle a product may not be formed under service conditions. An analysis of a typical blown oil sold as a road binder is given below for the sake of comparison with other oil residuums.

SEMIASPHALTIC BLOWN OIL RESIDUUM.

| Specific gravity, and/and C | 0 74 |
|--|---------|
| Specific gravity, 25°/25° C | .974 |
| Flash, degrees C | 260° |
| Melting point, degrees C | 55° |
| Penetration, 25° C., No. 2 N., 100 gms., 5 sec | 136° |
| Loss at 163° C., 7 hours | 0.18% |
| Loss at 205° C., 7 hours | 0.68% |
| Character of residue (dense, sticky, somewhat harder than origi- | |
| nal material). | |
| Soluble in CS ₂ , air temperature | .99.92% |
| Bitumen insoluble in 72° naphtha, air temperature | 16.36% |
| Bitumen insoluble in 86° naphtha, air temperature | 22.05% |
| Per cent of soluble bitumens removed by H ₂ SO ₄ | 25.16% |
| Per cent of soluble bitumens as saturated hydrocarbons | 74.84% |
| Bitumen insoluble in CCl ₄ , air temperature | 0.00% |
| Paraffin scale (strongly colored) | 5.1% |

Acid Sludge. — In the purification of certain distillates obtained from crude petroleums, sulphuric acid is often used to remove the unsaturated compounds. Sulphones and other complex compounds are formed and separated from the saturated hydrocarbon oils by subsidence. This material is known as acid sludge and often solidifies upon standing. It is usually considered a waste product, but is sometimes sold as a road binder. Such material, while possessing fair adhesive qualities,

is unsuited for use as a permanent binder owing to the fact that it is quite readily acted upon by water, being partially soluble and easily disintegrated.

Crude Oils. — While refined oils or oil residuums are usually of much greater value than crude oils for road treatment, the latter have been employed to some extent for this purpose, especially in California. The different characteristics of oils from the various fields have already been shown by analyses of their residuums and these residuums will be further discussed with reference to their suitability for road purposes. Before doing this, however, it may be well to briefly consider the crude petroleums. In general it may be said that the value of an oil for road purposes is directly proportional to the amount of true binding base which it holds or is capable of producing after application. Paraffin oils are wholly lacking in both respects and are, therefore, unsuited for road treatment. They may be employed solely as dust preventives, but being of an inherently greasy nature, they hold the dust down by force of capillarity only. If applied in any considerable quantity they form a slippery oily mud in wet weather, which is ruinous to clothes and the paint on vehicles, besides being extremely disagreeable to persons driving over the roads. Crude semiasphaltic oils are less objectionable, but can only be considered as temporary or at best as semipermanent binders. They possess the same chemically stable characteristics as the paraffin oils and after application are capable of developing a higher binding value only by volatilization of the lighter constituents under atmospheric conditions. A natural residuum may thus be produced in situ but it will always be more oily than sticky on account of the presence of a large amount of non-volatile fluid paraffin constituents. The truly asphaltic crude oils, on the other hand, are inherently adhesive and after application are capable of being gradually transformed under atmospheric conditions into almost true asphalts. This transformation is not entirely dependent upon evaporation, for the sulphur which is always present and probably atmospheric oxygen react to form nucleus condensation products in approximately the same way that many native asphalts are formed. A gradual hardening of the road surface, therefore, takes place and the mineral aggregate becomes more firmly bonded and consolidated.

It is not a difficult matter to distinguish between the crude asphaltic and paraffin petroleums, for the former are usually darker in color and much more viscous and sticky than the latter. This adhesiveness is particularly noticeable if a small quantity of the oil is rubbed between the thumb and forefinger until the greasy constituents are absorbed by the skin. When so tested, paraffin oils are completely absorbed, while the adhesiveness of the asphaltic oils becomes more pronounced.

The following table of analyses of crude oils, embracing the three types, paraffin, semiasphaltic, and asphaltic, serves to show some of their differences in properties. These results do not in any sense represent absolute values for the different classes, but will serve to give a general idea of the relative characteristics of each.

| CR | 1 | T | D | E | P | EΓ | r_{R} | 0 | T.F | 15 | TN | TS | |
|----|---|---|---|---|---|----|---------|---|-----|----|----|----|--|
| | | | | | | | | | | | | | |

| | Pennsylvania Paraffin. | Texas Semi- asphaltic. | California Asphaltic. |
|--|------------------------------------|---|--------------------------|
| Specific gravity, 25°/25° C. Flash, degrees C. Volatility at 110° C, 7 hours. Volatility at 160° C, 7 hours. Volatility at 205° C, 7 hours. Residue. Character of residue. | Ord. temp. 47.3% 58.0% 68.0% 32.0% | .914 43° 20% 27% 49% 51% Quick flow | .939 26° |

^{*} Volatility at 200°, 7 hours.

It will be noticed from the foregoing results that in the samples examined the specific gravity increases from the paraffin to the asphaltic oil. This is also true of the percentage of residue, while the volatility decreases correspondingly. The residues vary in character from soft and greasy through an intermediate and but slightly viscous nature to the more or

less liquid maltha of good adhesive properties. A rough idea of the character of these bases may be formed, as in the case of the crude oil, by rubbing a little of the residue between the finger and thumb. The color and odor will also indicate the character of the crude material to those familiar with the different varieties. In comparing the Pennsylvania with the Texas oil it will be seen that the former carries a higher per cent of light oils than the latter.

The characteristics of a crude oil which might almost be classed as a permanent binder are shown in the following analysis of a California road oil.

CALIFORNIA ROAD OIL.

| Characterblack, viscous | , sticky |
|--|----------|
| Specific gravity, 25°/25° C | 0.984 |
| Flash, degrees C | 160° |
| Loss at 100° C., 7 hours | 5.25% |
| Character of residueconsiderably more viscous than | original |
| Loss at 163° C., 7 hours | 16.4% |
| Character of residuesticky, very | viscous |
| Loss at 205° C., 7 hours | 30.0% |
| Character of residue solid but no | |
| Soluble in CS ₂ , air temperature | 99.77% |
| Organic matter insoluble | .12% |
| Inorganic matter | .11% |
| ī | 00.0 |
| Ditumon incoluble in 860 norththe air temperature | 9.8% |
| Bitumen insoluble in 86° naphtha, air temperature | , ,, |
| Fixed carbon | 2.05% |

Note. — This oil contained a small amount of water.

It will be seen from the volatility tests that this oil is capable of increasing greatly in consistency after application and would serve as an excellent binding medium.

Oil Distillates. — Oil distillates are but little used in the treatment of roads, except as fluxes for the heavier residual products. If employed in their natural state, they are of value as dust preventives only and should be applied sparingly, for they contain no true binding base and are inherently oily. They can only be considered as poor material at best in this

connection. These distillates are heavy in nature and have usually been treated for the extraction of solid paraffine.

The results of an examination of such an oil distillate are given below:

HEAVY OIL DISTILLATE.

| Specific gravity, 25°/25° C | 0.894 |
|-------------------------------------|----------|
| Flash, degrees C | 1000 |
| Burning point, degrees C | 155° |
| Viscosity at 25° C., degrees Engler | 3.3° |
| Loss at 163° C., 7 hours | 12.88% |
| Loss at 205° C., 7 hours | 25.60% |
| Character of residue Oil | y, fluid |
| Paraffin scale | 0.62% |

If such a distillate is heated at high temperatures in an open dish for a considerable length of time, a certain amount of solid residue will be produced. This residue, however, is not present in the original oil but is formed at the high temperatures by decomposition and cracking of some of the hydrocarbons present. When it is desired to ascertain the character of the base held by an oil, 205° C. should under ordinary conditions be the highest temperature employed. This material should, therefore, be considered as holding no true binding base.

Oil distillates have been employed in the manufacture of cutback products, but for this purpose should be quite volatile, in order that they may evaporate after application. Cut-back products are solid oil residues fluxed with distillates to any desired consistency. The distillate should serve merely as a carrying agent for the true binding residue and thus facilitate application, after which it should volatilize and leave the original residue in place. Such distillates as shown above are unsuited for this purpose because they are not sufficiently volatile, and any mixture in which they may be employed will maintain its original consistency indefinitely after application. Fluxes of this nature should be employed only to bring a hard bitumen to the consistency which it is desired to maintain on the road and for this purpose a fluid oil residuum is as a rule to be preferred.

Cut-Back Oils. — If a fluid cut-back product is to be used successfully as a binder in road construction, the distillate flux should be volatile at as low a temperature as possible. When heated in an open dish for five hours at a maximum temperature of 163° C., the preparation should produce a residue of the desired consistency and if it does not, there is little chance of the oil proving satisfactory under service conditions. Consistency of the residuum is of course not the only thing to be considered, but it is one of the most important to be noted after the chemical characteristics of the oil itself have been ascertained. Methods for determining these characteristics will be described in a later chapter.

The results of an examination of an excellent cut-back oil for road work are given below:

CUT-BACK ROAD OIL.

| CharacterViscous, sticky, fluid | |
|--|--------|
| Specific gravity, 25°/25° C | 0.942 |
| Flash, degrees C | 32° |
| Burning point, degrees C | 34° |
| Loss at 100° C., 5 hours | 18.63% |
| Loss at 163° C., 5 hours | 20.12% |
| Character of residue dense, semiasphaltic | |
| Penetration of residue, 25° C., No. 2 N, 100 g., 5 sec | 106 |
| Bitumen soluble in CS ₂ , air temperature | 99.90% |
| Organic matter insoluble | .08% |
| Inorganic matter | .02% |
| | |
| | 100.00 |
| Bitumen insoluble in 86° naphtha | 17.0 % |
| Fixed carbon | 6.64% |

From this examination it is evident that the product is a dense artificial asphalt which has been fluxed with about one-fourth its weight of a light volatile flux. The former fact is indicated by the character and penetration of the residue obtained from heating the oil at 163° C. and the latter by the loss at 100° C., the low flash and rather low specific gravity. In some respects a higher flash point would be more desirable. That

this material will quickly come to and be maintained at its maximum consistency is shown by the close agreement of the loss at 100° and 163° C. The high solubility in carbon bisulphide shows it to be an exceedingly pure bitumen and the high percentage of bitumen insoluble in 86° Baumé naphtha indicates very good asphaltic properties which have not been produced entirely by blowing, as shown by the medium amount of fixed carbon. The penetration of the residue indicates that the true binding base is of suitable consistency for road construction, and the high volatility and low flash that the original material must be applied without heating.

Fluid Oil Residuums. — The residuums of the various petroleums have been used to a great extent both as fluxes for the solid native bitumens and as substitutes for the same in the paving industry. Their various characteristics and properties have therefore been given considerable attention, and from the standpoint of road treatment, the results obtained from a study of these fluxes and artificial asphalts should be of service in determining the suitability of various oils for this purpose. The characteristics of the residues will naturally vary as the crude petroleums vary, although as has been shown they may be considerably influenced by the method of preparation.

The paraffin petroleum residuums are of a soft greasy character and, as their name implies, contain a large amount of paraffin hydrocarbons and paraffin scale or crude paraffin. A road surface treated with material of this nature will be dustless for the time being but in damp, rainy weather will become covered with a slimy, greasy mud which is easily washed away, leaving the road in as bad condition as it was before treatment, if not worse. Even when used solely as a flux for asphalt the paraffin scale is apt to cause bad results if present to the extent of over 10 per cent. When the crude or even the residual oil is used as a binder, it is, therefore, only to be supposed that the outcome will prove a failure. The base held by California petroleums is composed of bitumens resembling asphalt. The residuum as a rule contains no paraffin and if cracking has

not been employed in its preparation shows but little free carbon. As has been stated they are the most satisfactory type for use as dust preventives and road binders.

While the properties of the residuums produced by petroleums from the various fields have already been given, the differences can better be seen by a direct comparison. Three typical fluid oil residues are, therefore, shown in the following table:

FLUID PETROLEUM RESIDUES.

| Specific gravity, 25°/25° C | Pennsylvania Paraffin. 0.920 186° 5.3% | Texas Semiasphaltic. 0.974 214° 0.8% | California Asphaltic. |
|--|--|---|--|
| Character of residue Loss at 205°, 7 hours Character of residue Bitumen soluble in CS ₂ Organic matter insoluble Inorganic matter | Soft 14.2% Soft 99.8% 0.2% 0.0% | Soft 6.2% Soft 99.6% 0.4% 0.0% | Soft 17.3% Soft 99.7% 0.3% 0.0% |
| Bitumen insoluble in 88° naphtha Per cent of soluble bitumen removed by H ₂ SO ₄ Per cent of total bitumen as saturated hydrocarbons Paraffin scale Fixed carbon | 4.3% 21.9% 74.8% 11.0 | 4.8% 20.9% 79.4% 1.7% 3.5% | 7·7% 54·9% 41·9% 0.0% 6.0% |

In comparing these results an increase in specific gravities running in the same direction as those for the crude petroleums will be noticed. The flash point and volatility, however, are not graded. As they are of course due entirely to the point at which distillation is stopped, in the process of refining, this is only to be expected. As shown by the test for solubility in carbon bisulphide, these oils are practically pure bitumens. The material insoluble in 88° naphtha is found to increase from the Pennsylvania to the California oil, which indicates an increase in body of the oils. It will be noticed that a much

higher percentage of unsaturated hydrocarbons is present in the California oil than in the other two. The percentage of solid paraffins on the other hand decreases from the Pennsylvania to the California oil. The latter rarely contains any paraffin scale, while the former often holds as high as 30 per cent and over. The percentage of fixed carbon runs in the opposite direction and this, like the percentage of naphtha insoluble bitumen, indicates the relative amount of body forming hydrocarbons which tend to produce mechanical stability.

In comparing the crude oils with the residuums, it will be seen that, for the same type, the specific gravity and flash point of the former are lower and that the volatility is higher, as would naturally be expected. Other things being equal, therefore, the residual oils should be preferable for road treatment, because of the concentration of any binding base which may be present. In all cases, however, the use of truly paraffin oils should be avoided and those which more nearly approach the California type be given preference.

Owing to the method now commonly employed of piping crude oil from wells to the storage tanks, making use of the same line to carry oils from a great number and variety of wells, it is often a difficult matter to obtain two lots of oil showing the same properties, even when purchased from the same source. Added to this, the fact that at the present time the manufacturer is turning out a great variety of carelessly prepared road oils makes it very important that an examination of each lot be made before attempting to use it for road purposes. Many instances might be cited of road oils varying inexcusably in character, which have been sold under the same trade name as representing a definite product. Until certain standards are adhered to, it is, therefore, useless to give analyses of trade products as representing anything definite. The properties of certain fluid residual road oils as now found upon the market are, however, given in the table below in order to discuss their relative value as dust preventives and road binders.

FLUID RESIDUAL ROAD OILS.

| No | I | 2 | . 3 |
|---|-------------------------|--------------------|---------------------------------------|
| Character | Thin, greasy | Quite viscous, | |
| Specific gravity, 25°/25° C | 0.916 | Fairly sticky | 0.989 |
| Flash, degrees C | Too soft 8.86 | Too soft | 196° |
| Loss at 163° C., 5 hours | Fluid, granu- | 0.49 But little | o.04% Sticky, some- what harder |
| Penetration of residue (as above) Soluble in CS ₂ , air temperature | lar, greasy Too soft | Too soft | 142 99.77% |
| Organic matter insoluble | 99·75 ·25 o.oo | 0.0% | .05% |
| Inorganic matter | 100.0 | | 100.00 |
| Per cent bitumen insoluble in 86° naphtha, air temperature | | 5.12% | 20.02% |
| Fixed carbon | 4.26 | 4.73 | 11.53 |

From the above results it will be seen that oil No. 1 is a very fluid reduced or residual oil, as shown by its specific gravity, flash point and volatility. While probably semiasphaltic in character, it is rich in paraffin hydrocarbons, which fact is indicated by the granular appearance of the residue. Its naphtha insoluble bitumen and fixed carbon are low, indicating poor mechanical stability, and while its loss at 163° C. is fairly high, the fact that the residue is still fluid and greasy shows it to be incapable of developing good binding qualities under service conditions. As shown by its solubility in carbon bisulphide, this material is almost pure bitumen and the same is true of the other samples.

Sample No. 2 is a denser residuum whose flash point indicates that it has been distilled at a higher temperature than No. 1. This is also shown by the volatility test, the loss at 163° C. for five hours being less than half of 1 per cent. As in the case of No. 1, its low naphtha insoluble bitumen and low fixed carbon show it to be deficient in mechanical stability and the character of its residue, from the volatility test, incapable of

improving in this respect under service conditions. It is, however, somewhat sticky and capable of serving as a weak binder.

Sample No. 3 is a dense, viscous oil residuum almost semisolid in character as shown by the penetration test. Its very low loss when heated at 163° C. for five hours proves that it has been distilled at a higher temperature than either of the other two. Its sticky character indicates good binding qualities and its rather high naphtha insoluble bitumen and fixed carbon show a greater degree of mechanical stability, which is capable of being further developed under service conditions to some extent, this being indicated by the decrease in penetration of the residue from the volatilization test over the original material. Its high naphtha insoluble contents would tend to show that it is a partially blown oil.

From the foregoing it is evident that an increasing value for road binding exists from sample No. 1 to No. 3. The former can only be considered as a dust preventive at best, which has practically no value as a binder and is suitable only for surface application in small quantities. Owing to its fluid character it may be applied cold by means of a sprinkler. Sample No. 2 may be classed as a semipermanent binder suitable for surface application only and of little or no value for road construction. It should preferably be applied hot. Sample No. 3 may, on the other hand, be considered as a fairly good permanent binder, suitable for construction work where the mineral aggregate contains a sufficiently large quantity of coarse particles to produce a condition of stability independent of that of the binder. It should of course be heated before applying, and might then be satisfactorily employed according to the penetration method which will be described in a later chapter.

Semisolid and Solid Oil Residuums. — Blown oils and oil pitches or artificial asphalts constitute the semisolid and solid oil residuums. Most of those now on the market are semi-asphaltic in character and some few have been reinforced by the addition of a small amount of a solid native bitumen such

as gilsonite, for the purpose of increasing their body and binding value. They are employed largely as fillers for brick and block pavements, as roofing pitches, for sheet asphalt construction and also in the construction of bituminous macadam roads.

According to a recent report * of the Geological Survey, the production of oil asphalts in the United States for 1908 was 102,281 short tons, valued at \$1,322,616. In these statistics, apparently no attempt was made to distinguish between the blown oils and residual pitches, and the states of Cailfornia and Texas only were reported. The production of these states was as follows:

PRODUCTION OF OIL ASPHALT IN 1908.

| | Quantity. (Short tons.) | Value. |
|-----------------|----------------------------|-----------------------|
| CaliforniaTexas | 85,114 17,167 | \$ 972,176 350,440 |
| Total | 102,281 | \$1,322,616 |

Had the blown oil products of the mid-continent and southern Illinois fields been included, the totals would have been very materially increased, as the output from the former in particular is quite large.

When employed in road construction these materials should serve as permanent binders and add to the stability of the road. It is necessary to heat them before use and they should preferably be mixed with the roadstone before it is laid. They act as dust preventives only by reducing road disintegration and wear and do not act as dust layers. Examples of this class of products are given below. They are usually sold under the name of road asphalts.

^{* &}quot;Mineral Resources of the United States, Calendar Year 1908."

SOLID OIL RESIDUUMS.

| Character | Semiasphaltic Blown Oil. | Semiasphaltic Residual Pitch.* | Asphaltic Residual Pitch.* |
|--|-----------------------------|--------------------------------------|----------------------------------|
| Color | Dark brown | Black, lus- trous | Black, lus- trous |
| Fracture | Cheesy | Conchoidal | Conchoidal |
| Specific gravity, 25°/25° C | 0.995 | 1.070 | 1.071 |
| Penetration, 25° C., No. 2 needle, 100 | 1930 | 7° | 52° |
| gms., 5 sec | | .95% | 2.7% |
| Penetration of residue (as above) | 1360 | .95/0 | 200 |
| Bitumen soluble in CS ₂ , air temper- | 130 | | 29 |
| ature | 99.71 | 98.2% | 99.7 |
| Organic matter insoluble | | 1.8% | .3 |
| Inorganic matter | | Trace. | Trace. |
| | | | |
| | 100.00 | 100.00 | 100.00 |
| Bitumen insoluble in 88° naphtha | | 29.4% | 27.8 |
| Bitumen insoluble in CCl ₄ | | 14.6% | 6.0 |
| Fixed carbon | 11.8% | 19.5% | 18.8% |
| · , | | | 1 |

^{*} Taken from Richardson's "Modern Asphalt Pavement."

In regard to these products it may be said that the blown oil and asphaltic pitch might be used to advantage in road construction, but that the semiasphaltic pitch is too hard, as shown by its penetration. The blown oil is very considerably softer but capable of hardening with age. It is non-volatile at 163° C. but increases somewhat in consistency. The percentage difference in penetration of the residue as compared with the original sample is not so pronounced as in the case of the California pitch, which is an advantageous feature in a material of sufficient original consistency to serve as a strong road binder. It has been carefully prepared, as indicated by the complete solubility of its bitumen in carbon tetrachloride. The same can hardly be said for the asphaltic pitch, as it carries six per cent insoluble in this solvent. The semiasphaltic pitch has been quite badly cracked, as it contains 1.8 per cent organic matter insoluble in carbon bisulphide and 14.6 per cent insoluble in carbon tetrachloride.

The advantages of a good residual pitch over a blown prod-

uct are that its binding power is greater, it shows greater ductility and if properly prepared is less subject to changes by weathering. A blown oil, on the other hand, while being characteristically short or non-ductile, is less susceptible to temperature changes; that is, at extremes of heat and cold its physical properties do not greatly vary. The asphaltic pitches, if moderately hard at ordinary temperatures, are apt to be brittle in cold weather and soft in hot weather. Under proper conditions both materials should give good service as road binders.

Petroleum Emulsions. — Emulsions of petroleum with water may be made either by mechanical or chemical means. Chemical emulsions have been most generally used in road treatment, but before considering them it may be well to mention an apparatus which has lately been devised for the purpose of forming and spreading a mechanical mixture of oily substances and water upon a road surface. This is a cart known as the "Emulsifix," fitted with two tanks, one containing the oil and the other water. These two substances are led through pipes into a box where they are thoroughly mixed by means of rapidly whirling blades which also force the mixture upon the road in the form of a fine spray. The water either evaporates or is rapidly absorbed by the road, leaving the oil in a fine film over the surface, where it acts as a dust layer and temporary binder.

Chemical emulsions are oily substances made miscible with water through the agency of saponifying materials, such as caustic soda, potash and ammonia. Petroleum will not saponify directly to any extent with these alkalies and recourse must be had to some animal or vegetable fat which will react with the saponifying agent to form a soap solution with which the mineral oil will emulsify. Commercial oleic acid, known as elaine, and cotton-seed oil are most commonly employed for this purpose to the extent of approximately three per cent by weight of the oil. Carbolic acid, pine oil and various other materials are sometimes used in the preparation of these emulsions both for the purpose of assisting the process of emulsifica-

tion and to neutralize or destroy any objectionable odor which the oil may have.

In 1903 and 1904 road oil emulsions first made their appearance in France and Germany and since then have been employed to some extent in this country. They are sold in concentrated form as viscous, oily liquids which should be mixed with a considerable amount of water before being applied. they contain a good semiasphaltic oil, they not only serve as dust layers, but as semipermanent binders, and as they have to be applied at frequent intervals, often produce an accumulation of oil on the road surface which binds the fine particles of roadstone together and materially protects the road from wear. If the oil is of a paraffin nature, however, the same objections may be urged against its use as were made in connection with the use of crude paraffin oils, the only difference being that when emulsified the oil may be applied in such a thin coat that the undesirable properties are not so obvious. Such emulsions act as dust layers only and not as road binders. Some of the heavier asphaltic emulsions have, however, been sold as permanent binders for use in road construction.

An objection which has been offered to the use of petroleum oil emulsions is that being originally miscible with water the oil is apt to be washed out of the road after application by rains. This is true to only a limited extent, as the emulsified condition is a very unstable one, the oil and water being in a rather delicate state of equilibrium which may be readily destroyed, thus causing a separation of the oil and water. Prolonged and violent agitation will cause this to occur and also the sudden introduction of any solid matter in a finely divided state. Thus a handful of sand thrown into one of these emulsions will often cause the oil and water to separate almost instantaneously and once separated, it is difficult to make them mix again. It is very probable that such a separation takes place when an emulsion strikes a road surface and this would account for the retention of the oil by the road even when subjected to long spells of rain. Because of this, a road which

has been treated for a season with a good emulsion will at the end of that time often have the appearance of having been recently treated with a semipermanent oil binder. Volatile emulsifying agents such as ammonia are to be preferred to the fixed alkalies not only because a more complete separation is effected upon the road surface, but also because the character of the oil is less likely to be injured.

The characteristics of two typical emulsifying road oils are given below:

| EMULS | SIFYING | ROAD | OILS. |
|-------|---------|------|-------|
|-------|---------|------|-------|

| Emulsion No | I | 2 |
|---|--|---|
| Characteristics. Specific gravity, 25°/25° C. Volatilization: Loss at room temperature, 24 hours Additional loss at 100° C., 5 hours Character of residue. | Greasy 0.923 3.23% 12.31% Thick, greasy, | Sticky 0.986 10.77% 11.05% Semisolid, sticky |
| Determinations made on samples dried at 100° C.: Soluble in CS ₂ , air temperature | 2.61% | 97.98% 1.63% .39% |
| Insoluble in 86° naphtha, air temperature Fixed carbon | 5.09% 1.17% | 10.68% |

Remarks. — The naphtha insoluble material from No. 1 was a saponified jelly like mass, with but little evidence of the presence of residues obtained in like manner from asphaltic oils. That obtained from No. 2 was asphaltic in character.

From the above results it is evident that No. 2 is greatly superior in road binding value to No 1. The former contains an excellent semiasphaltic oil residuum, while the latter carries a relatively light oil very rich in paraffin hydrocarbons.

In some instances experimenters have prepared oil emulsions for their own use by mixing a solution of common soap with the oil according to an old recipe known as Cook's formula. The parkways in Boston and Chicago have for the last few years been treated with such emulsions made under the supervision of the park superintendent. In the former case ten to fifteen pounds of cotton-seed oil soap are first dissolved in fifty gallons of water by the aid of steam heat. To every fifty gallons of soap solution one hundred gallons of semiasphaltic oil are added and emulsified through agitation by a steam pump. This forms a stock solution containing 66 per cent of petroleum, which is further diluted with water before application.

In Lincoln Park, Chicago, a mixture of Kansas and California oils is emulsified. In this case a naphtha soap is employed because it is found to work best with the hard lake water. The process of emulsification is described by West * as follows: "The mixing plant consists of a series of three twohundred-gallon hogsheads, set close together on end with their top heads removed. The hogsheads are connected at the bottom with three-inch pipe having gate valves. In each of these receptacles are pipes for live steam and for cold water. From the bottom of the hogsheads connecting pipes lead to a steam pump of about forty gallons capacity. Arrangements are made so that the material can be pumped through any one of the hogsheads back into the same or other compartments through a reduced nozzle; or so that the material may be pumped from the oil delivery wagon to any of the receptacles; or from any of the receptacles into a sprinkler, which is used in applying the emulsion to the road.

"In making the emulsion, sixty gallons of water are drawn into two of the hogsheads, the third hogshead being disconnected and reserved for heating water for subsequent use. Live steam is then turned on, and the water brought to its boiling point. Fifteen pounds of soap are then added and the water allowed to boil five minutes longer. Sixty gallons of the Kansas oil are then added, and the mixture allowed to pass out of the bottom of one hogshead, through the steam pump back into the top of hogshead number two, through the agi-

^{*} Good Roads Magazine, November, 1907, "Oil Emulsions for Macadam Roads."

tating hose for about five minutes, when one-half barrel of California asphaltum is added, and the whole mixture allowed to emulsify for twenty minutes longer. It is then pumped into a distributing sprinkler of eight hundred gallons capacity, fitted with an adjustable cup discharging attachment. After receiving the stock solution the sprinkler is filled to its capacity with boiling water."

Summary and Conclusions. — In this chapter the production and characteristics of petroleums, together with their products of manufacture which are of interest from the standpoint of road treatment, have been reviewed. The supply of petroleum being at the present time almost unlimited and the properties of many of these oils being suitable for this purpose, it is evident that oil and oil products will for a long time continue to be an important factor in dust prevention and road preservation. the properties of different oils vary within wide limits and as some are totally unfit for road purposes, it is most necessary that an examination or analysis be made before selecting a product for any considerable amount of work. The use of oils and their methods of examination are treated in other chapters, which should be closely associated in the reader's mind with the foregoing in order to obtain a correct idea of the value of results of the analyses as given in the preceding tables.

CHAPTER IX.

SEMISOLID AND SOLID NATIVE BITUMENS.

THE semisolid and solid native bitumens of interest from the standpoint of road treatment include the natural malthas. so-called rock asphalts, genuine asphalts, gilsonite and grahamite. As a class they represent the most permanent type of road binders, but only serve as dust preventives by reducing the wear of roads in which they are employed. Some of them have been employed for many years in the construction of sheet asphalt pavements. It does not come within the scope of this book to consider them in this connection, and as a number of standard textbooks dealing with the construction of this type of pavement have been published, it is unnecessary to so treat them. Their adaptability for road treatment and construction especially will, therefore, be made the subject of this It should be remembered, however, that their use for this purpose is the connecting link between the suburban road and the city pavement, and an overlapping of the two subjects at this point is almost inevitable as no sharp dividing line can be drawn between them.

Malthas. — Malthas or, as they are sometimes called, mineral tars, are very viscous semiasphaltic or asphaltic substances, holding, as has been stated, an intermediate position between the petroleums of an asphaltic nature and the true asphalts. Some are probably the direct products of natural distillation of organic materials and some have been formed by the natural evaporation and oxidation of certain petroleums. They are usually black or brown black in color and range in specific gravity from 0.95 to 1.00 and slightly higher. Some are so nearly solid that they can be drawn into threads. They resemble certain

artificial petroleum residuums in some respects but contain a larger proportion of volatile hydrocarbons, and when moderately heated are converted into harder material. Because of this they are little suited for use as fluxes for the harder bitumens but should prove serviceable in the treatment of roads, as their binding qualities improve with age under service conditions. They are in fact slowly transformed into a species of asphalt upon exposure to the atmosphere both by evaporation and oxidation.

Most of the maltha exploited in this country is found in California. During 1908 this state produced 12,579 short tons valued at \$158,520 out of a total for the United States of 12,875 tons valued at \$162,000. Oklahoma produced the remaining 116 tons valued at \$3,480. There is little data to be had relative to the physical and chemical characteristics of the malthas, but the following analysis of a California product as given by Richardson * gives some idea of their general properties.

CALIFORNIA MALTHA.

| Specific gravity, 25°/25° C | 0.9867 |
|----------------------------------|--------|
| Flash point, degrees C | 1180 |
| Loss at 163° C., 7 hours | 7.0% |
| Loss at 205° C., 7 hours | 28.0% |
| Penetration of residue | 40° |
| Bitumen insoluble in 88° naphtha | 6.7% |

The malthas often contain gas and water and when heated froth violently. According to Peckham some of the water appears to be chemically combined as water of hydration of certain basic oils present in the maltha. This, however, has not been definitely proven.

Rock Asphalts. — Rock asphalt or bituminous rock is the term applied to a great variety of sandstones and limestones more or less saturated with maltha. In reports of the Geological Survey it is also made to apply to asphaltic earths and shales. The rock may be either friable and wholly dependent

^{* &}quot;The Modern Asphalt Pavement," Second Edition, p. 129.

upon the bitumen to hold the individual mineral fragments together or it may be solid, merely having its interstices filled with bitumen. Deposits of such materials are widely distributed over the United States, but are found principally in California and Kentucky. The output in short tons in 1908 for these states was as follows:

PRODUCTION OF BITUMINOUS ROCK IN 1908.

| State. | Quantity. | Value. |
|------------------------|------------------|--------------------|
| California Kentucky | 27,118 10,253 | \$91,998 54,823 |
| Total | 37,371 | \$146,821 |

Taff* describes the occurrence of bituminous rock in the United States as follows:

"Extensive deposits of asphaltic shale and sandstone are found in California in and contiguous to the oil fields from the vicinity of Santa Cruz southwestward, generally parallel with the coast. Bitumen permeates porous sandy strata and exudes at the surface from highly bituminous oil-bearing deposits, and is found in smaller quantities in veins cutting the same class of rocks. The asphalt in this region appears for the most part to be a residue by natural distillation at or near the surface of the earth from the same crude oil that yields the oil asphalt.

"Utah contains large deposits of both asphaltic limestone and sandstone. Those probably of greatest purity and highest quality are the asphaltic limestones in the vicinity of Indian and Lake canyons in Strawberry Creek valley, Wasatch County; on Tie Fork of Soldier Creek northwest of Tucker, on the Rio Grande Western Railroad, Utah County; and between Soldier and Diamond creeks, a few miles northeast of Thistle Junction,

^{* &}quot;Mineral Resources of the United States, Calendar Year 1908." U. S. Geological Survey,

in the same county. Bituminous rock deposits are also reported from the same vicinities south of Thistle Junction. Similar deposits of bituminous limestone are known near the head of Whittemore Canyon north of Sunnyside, in Carbon County. In the Strawberry Creek valley especially the bituminous rock seems to be associated with veins of wurtzelite, and it is probable that the asphalt contained in the limestone partakes of the nature of wurtzelite or gilsonite. The natural asphalt that exudes from the bituminous rock of certain localities in Wasatch and Carbon counties is noticeably tenacious and elastic. Bituminous sandstone is reported in Uinta County east and northwest of Jensen, and in the Book Cliffs toward the source of Willow and Whittemore creeks in Carbon County. These bituminousrock deposits are flat lying and are usually accessible from the sides of the canyon and valleys. All the bituminous-rock deposits of Utah at present known are contained in formations of Tertiary or later age, and occur in or near the boundaries of the Uinta Basin.

"Extensive deposits of bituminous rock of variable richness are found in Oklahoma. Flat-lying strata of bituminous sand occur in eastern Stephens, in Jefferson, in Comanche and in Carter counties in late Carboniferous strata. Notable deposits also occur near Loco and Asphaltum, and asphaltic sandstones, more or less steeply inclined, are found in Carboniferous rocks near Woodford, Ardmore, Overbrook, Buckhorn and Fitzhugh. Bituminous sandstone and limestone in large quantity and of considerable richness, impregnating rocks of Ordovician age, are found at Gilsonite and near Sulphur and Dougherty, in Murray County.

"Bituminous rock is found in Texas as asphaltic sand and limestone, occurring in the basal Comanche rocks in Burnett County, near the town of Burnett, and in Montague County, near St. Joe; as asphaltic limestone of Cretaceous age in Nueces County; and as asphaltic limestone in Uvalde County — which appears to be of better quality and of more interest at the present time than the bituminous sandstone found elsewhere in

Texas. This limestone is very porous, and the interstices and cavities contain a semisolid asphalt.

"The asphalts of Kentucky occur as bituminous impregnations of flat-lying Carboniferous sandstones, chiefly in the western part of the state, in Breckenridge, Grayson, Edmonson, Warren and Logan counties, and in Carter and Floyd counties in the northeastern part.

"Asphaltic sandstone of possible commercial value is found in southwestern Wyoming in Sec. 15, T. 15 N., R. 118 W. This bed is six feet thick, and its areal extent is not known. Another asphaltic sandstone of similar quality and of the same thickness occurs in the Bighorn Basin, in northern Wyoming, Secs. 28, 29, 32, and 33, T. 52 N., R. 89 W.

"Asphaltic sands of Comanche (Lower Cretaceous) age occur in Arkansas near Wolf Creek, Pike County. Bituminous sandstones of Carboniferous age have been developed locally in Missouri in the vicinity of Higgins Valley, Lafayette County, and in northern Alabama, but their commercial values are not known. Bituminous rock in Georgia has been reported from Fulton County. Presumably for trade reasons, bituminous deposits are not exploited in these states at the present time."

Rock asphalt has been employed to a considerable extent in the surfacing of macadam roads, but it is not all suitable for this purpose as both the character and percentage of bitumen present vary within rather wide limits. Thus some are comparatively solid rock carrying only one or two per cent of maltha, while others are loosely compacted sand deposits, the individual grains of which are bound together by the bitumen, which may run from three to nineteen per cent. The maltha itself may be either semiasphaltic or asphaltic, the latter of course being preferable. When separated from the bitumen the mineral aggregate will also vary greatly in different specimens. As a rule it is not properly graded for the construction of sheet asphalt surfaces and the bitumen is seldom of the right consistency for this purpose. As the serviceability of a sheet asphalt wearing surface is dependent upon the grading of the

aggregate, the consistency of the bituminous binder and the percentage of this binder within comparatively narrow limits, it is evident that the occurrence of a suitable combination of these properties in nature must be rather exceptional. For road work, however, the limitations are much broader and many of the rock asphalts may be employed to advantage.

Kentucky rock asphalt has been quite extensively exploited in the last few years for use in macadam construction and in many cases has produced excellent results. It is a fine grained sandstone impregnated with a sticky semiasphaltic maltha averaging from 6 to 8 per cent with a maximum of 12 per cent. It is found in pockets rather than in direct continuous veins, the distribution of the bitumen throughout the pocket ranging from a mere trace to saturation.

The quarrying and first crushing of rock asphalt are not unlike that of other rocks intended for macadam work. After being broken in pieces to pass a two-inch ring, it is conducted to a series of roll crushers, consisting of parallel steel cylinders, the bitumen in the rock producing sufficient adhesion to carry the material through the rolls once it has been forced against them. The finished product after crushing should consist of an aggregation of individual grains of sand, each thoroughly coated with a film of bitumen which should cause it to adhere firmly to the surrounding grains if subjected to pressure. chilled after compaction the mass becomes very hard and tough. If warmed in the hand the bitumen becomes semifluid and the whole mass mobile. It is this property which makes it possible to apply rock asphalt in warm weather as a binder for a macadam road. With age the bitumen hardens into a more asphalt-like substance in the same way that all malthas harden when exposed to the atmosphere.

The properties of a rock asphalt suitable for road purposes are shown in the following table, and the application of such material will be described in the succeeding chapter.

KENTUCKY ROCK ASPHALT.

| Bitu | minous | mate | rial | remov | red by | CS ₂ , | air | temp | erat | ure. | | 6.7 | 3% |
|------|-----------|-------|-------|--------|--------|-------------------|------|------|------|------|------|-------|----|
| | eral agg | | | | | | | | | | | 93.2 | 7% |
| | Retaine | d on | 10 | mesh | sieve | | | | | | | 1.0 | |
| | " | " | 20 | " | 66 | | | | | | | 3.0 | |
| | " | " | 30 | " | 44 | | | | | | | 5 · 5 | |
| | 66 | " | 50 | " | 66 | | | | | | | 43.0 | |
| | 46 | " | 80 | " | " | | | | | | | 35.0 | |
| | " | " | 100 | 56 | 66 | | | | | | | 4.5 | |
| | " | 44 | 200 | " | " | | | | | | | 4.5 | |
| | Passing | 200 | mesh | ı siev | e | | | | | | | 3.5 | |
| | | | | | | | | | | | I | 00.0 | |
| | ific grav | | | | | | | | | | | | |
| | at 163° | | | | | | | | | | | | - |
| | racter of | | | | | | | | | | | | |
| | men sol | | | | | | | | | | | | |
| | nic mat | | | _ | | - | | | | | | | |
| - | ganic m | | | | | | | | | | | | 6 |
| | 5 | | | | | | | | | | | | _ |
| | | | | | | | | | | | | 100.0 | 0 |
| Per | cent of | bitun | nen i | nsolu | ble in | 86° 1 | naph | tha. | | | | 17.9 | % |
| | d carbo | | | | | | | | | | | | |

Asphalts. — The true asphalts and other solid native bitumens of an asphaltic nature are of interest in the treatment of roads only in combination with bitumens of a fluid nature. They are too hard to be employed in their natural state but when fluxed with the proper amount of a suitable oil residuum, produce asphaltic cements of excellent binding character.

Natural asphalts do not occur in the United States to any great extent, but small quantities are found in California and have in the past been exploited. The greater part of the asphalt imported to the United States comes from Trinidad although considerable quantities come from Bermudez, and smaller amounts from Maricaibo, Cuba and Mexico. Domestic oil asphalts are supplanting them to some extent and competition is keen owing to the lower price although sometimes inferior quality of the domestic product. Imported asphalts are for the most part employed in the construction of street

pavements although lately some attempt has been made to utilize them for road work.

Trinidad asphalt occurs in two forms, known as lake pitch and land pitch, which differ somewhat in properties but originate from the same source. The lake pitch occupies what is thought to be the crater of an extinct mud volcano while the land pitch occurs in layers which were supposedly produced by overflows from the lake. The pitch lake has an area of something over 100 acres and is of unknown depth. Borings have been made to a depth of 135 feet at the center with no indication of having reached the bottom of the deposit. The estimated minimum available tonnage of asphalt in this lake is 9,000,000 tons. During 1908 over 92,000 tons of this material were imported into the United States together with nearly 6,000 tons of land pitch.

The crude lake asphalt is a uniform cheesy mixture of gas, water, fine sand, clay and bitumen, carrying about 39 per cent of the latter constituent. It flows slowly and excavations made in the lake gradually fill up. In the refined product the bitumen amounts to about 56 per cent and is a black, lustrous pitch having a specific gravity of 1.06 to 1.07. It contains a large percentage of sulphur and some nitrogen, but little or no oxygen. In common with other asphalts no solid paraffins are present but saturated hydrocarbons of the C_nH_{2n-2} series have been found. Polycyclic polymethylenes similar to those contained in the asphaltic oils are present in the lighter portions soluble in petroleum ether, and extremely complex unsaturated hydrocarbons make up the bulk of the naphtha insoluble material. Further physical and chemical characteristics of this and other asphalts will be found in the table of solid native bitumens on page 191.

Trinidad land asphalt differs from the lake product in the fact that it is very much weathered being denser and harder than the latter. It is of much less importance commercially and need not be considered further than to state that the addition of about fifty per cent more of a given flux is required to

bring it to the consistency of an ordinary asphaltic cement than in the case of the lake pitch. It is not as uniform as the lake product and has not proved as serviceable.

Bermudez asphalt is obtained from a shallow pitch lake formed by the overflow of soft pitch from several springs. The asphalt hardens slowly upon exposure and evolves gas. It does not, however, retain as much of this gas as the Trinidad product and carries a much smaller quantity of mineral matter. In fact the original pitch as it exudes from the springs is an extremely pure bitumen. It contains sulphur but in less quantity than the Trinidad. The deposit extends over an area of nearly 1000 acres and is in many places covered with a rank vegetable growth which is burned from time to time and consequently hardens the asphalt in its vicinity. The crude material as it is taken from the deposit carries from 10 to 46 per cent of water, from 0.5 to 3.6 per cent mineral matter and from 0.6 to 6 per cent adventitious organic matter, gas, etc. The refined asphalt varies in character to a greater extent than the Trinidad product. It contains about the same percentage of unsaturated hydrocarbons as the latter but a higher percentage of volatile constituents. There has in the past been much discussion as to the relative merits of the two asphalts for street paving. Both materials when properly employed have produced excellent pavements and in many respects there is little choice to be made in favor of one or the other. This is certainly true as regards road work where the refinements of construction in city paving are not encountered. It is improbable that either asphalt will ever be extensively employed for this purpose owing to their high cost and to the fact that the cheaper domestic oil asphalts and tar pitches will be found satisfactory.

Other varieties of asphalt such as the Maracaibo, Cuban, Mexican and California are of minor importance compared with the Trinidad and Bermudez products. Their approximate characteristics are, however, shown in the table of the solid native bitumens. None of these materials are likely to play an important rôle as dust preventives or road binders in this

country and they are mentioned as being only of passing interest. They all possess excellent road binding characteristics and may undoubtedly be employed to advantage in localities near which they are found.

Asphalt Refining. — Before they can be used commercially; crude asphalts must be treated for the removal of water and other impurities. This is accomplished in a very simple manner by heating the asphalt until the water and gases have been driven off, skimming off any vegetable matter which may rise to the surface of the melted material and in some cases removing the coarser mineral particles which may settle to the bottom. Some of the more volatile hydrocarbons are also removed by this treatment. When the mineral matter is in a very finely divided state and difficult to remove as in the case of Trinidad asphalt, it is allowed to remain, and acts as a filler in the construction of sheet asphalt pavements. While it may prove of service for this purpose, it can only be considered as a natural adulterant, of little or no value in connection with road work where no particular attempt is made to reduce the voids to a minimum.

. The refining process is conducted in two ways known as the fire method and the steam method. In the former, the crude material is placed in an open iron tank or melting kettle resting upon an arch of brick and heated by means of a free fire. In the steam method the asphalt is heated with superheated steam in a large rectangular tank fitted with coils or gangs of pipe. By this means the temperature of the asphalt can be readily controlled and the danger of overheating and cracking by the fire method is overcome. In either case the mass is kept agitated by a current of air or steam. When all the water has been driven off the process of refining is finished and the melted asphalt is drawn off into barrels which have been clayed on the inside to prevent it from sticking. This makes it possible to strip off the staves without difficulty when being used. About four days are required to complete the refining operation by the fire method and cracking is never entirely prevented no matter how

carefully the kettle has been fired. The steam method on the other hand consumes only twenty-four hours. If air is employed for the purpose of agitation a condition of affairs very similar to that described under blown oils is brought about and as might be expected certain oxidized and condensed hydrocarbons are formed which may strongly affect the character of the product. Steam agitation on the other hand causes the volatilization of a larger proportion of the lighter hydrocarbons.

Gilsonite. — Gilsonite is a very pure solid native bitumen, having a specific gravity of from 1.044 to 1.049. It is the most abundant of all of the solid native bitumens found in the United States, but its occurrence in commercial quantities is apparently limited to Utah and Colorado. It is found principally in the former state and is sometimes called Utah asphalt. In 1908 this state produced 18,533 short tons valued at \$61,824.

It is differentiated from the natural asphalts by being almost entirely soluble in carbon bisulphide and showing the presence of but little mineral matter. It is more brittle than the asphalts and much less soluble in 86 °B. naphtha. It also has a higher softening or melting point. The lighter products contained in gilsonite are composed almost entirely of unsaturated compounds, while, as has been stated, the corresponding constituents of the asphalts are for the most part saturated hydrocarbons.

Gilsonite has been successfully employed in the paving industry and is of considerable interest from the standpoint of road treatment, as a number of road preparations are now upon the market which contain it as a binding base. It of course has to be combined with an oil flux before it can be made suitable for use in this connection. Being an extremely pure bitumen it does not have to be refined, but is disposed of just as it is taken from the veins in which it occurs. It is sold in two grades, firsts and seconds, the former consisting of large lumps free from powder and the latter of smaller and more powdery material. It is employed to a considerable extent in the manufacture of japans, paints, varnishes, electric insulations, acid fume proofing, etc. where it is prized for the smooth, elastic,

resistant and durable coating which it produces. Its physical and chemical properties are shown in the table of solid native bitumens.

Grahamite.—Grahamite like gilsonite is a very pure solid native bitumen. It is black and brittle and does not melt readily but intumesces at high temperatures. It is found almost exclusively in Oklahoma, although a small quantity has been found in Coloorado. It was first discovered in West Virginia but the available supply in this state has become exhausted. In 1908, 2,286 short tons valued at \$20,340 were produced in Oklahoma.

Grahamite is differentiated from gilsonite and the native asphalts by the fact that it is almost completely insoluble in naphtha. It is far less soluble in carbon tetrachloride than either of the other classes of material, which as in the case of oil pitches is an indication that high temperatures have played an important part in its production. It is not as uniform in composition as gilsonite, and some varieties approach very closely the pyrobitumens in character and are known as asphaltic coals. It is probably composed almost entirely of unsaturated hydrocarbons.

Some varieties of grahamite have proved satisfactory in paving work when properly fluxed, and good results would probably be obtained by its use in road construction, although to the author's knowledge it has never been employed to any extent for this purpose. It has been used in the manufacture of paints, rubber substitutes and fillers for brick and block pavements.

Comparison of the Solid Native Bitumens. — Some of the differences between the various types of solid native bitumens have already been noted, but before leaving this subject it may be well to consider these differences in greater detail as they often have a direct bearing upon the proper method of preparing and handling mixtures suitable for paving and road work. The approximate chemical and physical properties given in the table on page 191 have been taken from reports on the examination of typical samples of the various materials, and show the principal

differences as effecting their use for the purposes above mentioned. It should, however, be remembered that the solid native bitumens must always be modified before use and that by treating in a slightly different manner, materials which are originally quite dissimilar, can often be made into finished products exhibiting very similar properties.

In this table it will be noticed that the specific gravities of the solid native bitumens are for the most part dependent upon the amount of mineral matter which they contain. Thus Trinidad asphalt carries the highest per cent of mineral matter and has a specific gravity of 1.40, while gilsonite being a practically pure bitumen has a specific gravity of only 1.04. The other materials fall into line between these two almost in the order of their decreasing mineral matter contents or as their solubility in carbon bisulphide increases. Although not shown in the table, it should be noted that the fracture of grahamite differs materially from all of the rest, being hackley while the others show a conchoidal or semiconchoidal fracture. The loss by volatilization at 163° C. and 205° C. is low in nearly every case but that of the Mexican asphalt. This would naturally be expected in any solid bitumen. The penetration results show that Bermudez has a little softer consistency than Trinidad, and that the Mexican is much softer than any of the others. The reason for this is apparent in their greater volatility. The per cent of bitumen soluble in 88° B. naphtha is found to vary considerably among the different materials, falling from 75 per cent in case of the Mexican asphalt to practically zero in the case of grahamite, which is characteristic of the latter. These naphtha soluble bitumens have been termed malthenes by Richardson and the naphtha insoluble, asphaltenes. The significance of these terms will be discussed in a later chapter, but for the present it may be said that the relation of one to the other will often have a very important bearing upon the treatment of solid bitumens in the preparation of asphaltic cements. amount of unsaturated hydrocarbons present in the naphtha soluble bitumen has been found to lie between 50 and 60 per

SOLID NATIVE BITUMENS.

| | Grahamite. | I.I Intumesces Intumesces 0.1% 0.1% 0.5% 100.0 100.0 100.0 100.0 100.0 100.0 100.0 100.0 100.0 100.0 100.0 |
|---|-------------------|--|
| | Gilsonite. | 1.04 1127°-149° 135°-163° 0.4-7% Smooth 1-2% Smooth 99.5% 0.0% 100.0 46% 0-0.4% |
| | California. | 1.06 77° 82° 0-27° 7% Smooth 20% Blistered 90.0% 3.0% 7.0% 7.0% 0.3% 0.3% |
| | Mexican. | 1.04-1.12 16°-140° 2-5% 13% 13% 0.5-20.0% 25-45% |
| | Cuban. | 1.30 1100 1100 170 Cracked 1.5% Wrinkled 75.0% 3.5% 21.5% 100.0 |
| | Maracaibo. | 1.07 99° 105° 25° 27° 8mooth 5% 95.0% 2.0% 3.0% 1.00.0 48% |
| 1 | Bermudez. | 11.07 74° 80° 15° 3% Smooth 8% Wrinkled 95.0% 2.5% 100.0 31% 0.6% 14% |
| | Trinidad Lake. | 1.40 88° 88° 88° 10° 80° 10° 30°50° 30°50° 30°50° 30°50° 30°50° 30°50° 30°50° 30°50° 31°60° 31°60° 31°60° 31°60° 31°60° 31°60° |
| | Variety. | Specific gravity, 25°/25° C Softens, degrees C. Flows, degrees C. Penetration at 25° C Loss at 163° C., 7 hours. Character of residue. Loss at 205° C., 7 hours. Character of residue. Loss at 205° C., 7 hours. Character of residue. Bitumen soluble in CS₂. Organic matter insoluble in Rer cent bitumen insoluble in 88° naphtha. Per cent bitumen insoluble in CCJ Carbon. Sulphur. |

cent in nearly every case but that of gilsonite, which is characteristically high, being about 82 per cent. The carbon tetrachloride insoluble material is low in every case but that of grahamite which is an indication that only the latter has been produced at excessive temperatures. The percentage of fixed carbon has no direct significance other than that it is often an identifying characteristic. This is particularly true of grahamite, which shows from 40 to 50 per cent. The Cuban asphalt is also characteristically high in fixed carbon. It should be noticed that the Cuban asphalt carries more sulphur than any of the others.

Asphaltic Cements. — In order that they may be employed in street paving it is necessary that the solid native bitumens be cut or fluxed with an oily body until sufficiently soft when heated to be incorporated with the mineral aggregate and to produce with this aggregate a mixture which while having sufficient rigidity, when laid, to withstand displacement under traffic, will not be so hard and brittle as to crack under service conditions. Such a combination of asphalt and oil produces an asphaltic cement.

An asphaltic cement for paving work should be prepared with a flux which is both chemically and physically stable in order that it may not be subject to marked permanent changes during or after application. The solid bitumen itself is relied upon to give the cement its binding properties and the flux acts mainly as a softening agent. Petroleum residuums have been almost exclusively used for this purpose, and many of these residuums, which by themselves would prove absolutely unfit for any sort of road treatment, are well adapted for the preparation of asphaltic cements. Thus the paraffin residuums when not too rich in paraffin scale have been successfully utilized as fluxes for the asphalts. Residuums which will harden after application, while in themselves suited for road treatment, will not prove satisfactory as fluxes in the preparation of ordinary asphaltic cements as the cement itself will then rapidly become too brittle after being mixed with the mineral aggregate. Specifications for fluxes usually require that when heated for seven hours at 325° F. (163° C.) the flux shall not volatilize more than 5 per cent of oil and that it shall be soluble in 88 degrees naphtha to not less than 90 per cent. The latter clause is inserted in order that the so-called malthenes and asphaltenes may be kept in normal proportions, without the use of an excessive amount of the flux.

In the preparation of road binders from the solid native bitumens, the same kind of flux employed in the paving industry should be used when it is desired to secure a binder whose normal consistency is to be maintained after application. A greater amount of the flux can, however, be employed in the preparation of these binders as it is possible to employ a much softer asphaltic cement with a coarse mineral aggregate, such as occurs in a road, than with the sand aggregate of the sheet asphalt pavement.

In some instances it is desirable to make use of a binder of softer consistency than should be permanently maintained, in order that it may be applied easily. When this is the case a partially volatile or self-hardening flux should be employed which will cause the binder to become harder after application. Such asphaltic cements are quite comparable with the cut back oil products mentioned in the preceding chapter.

Asphaltic cements employed in the paving industry are prepared as follows: A weighed quantity of the solid bitumen is melted in a suitable tank and brought to a temperature of about 163° C. A predetermined proportion of flux which has by trial been found to produce a cement of the desired consistency is then run into the melted bitumen. The flux is previously heated to about 95° C. and is added slowly, the mixture being meanwhile agitated by a current of air or dry steam. Agitation is continued until the solid bitumen and flux are thoroughly incorporated, from three to eight hours being ordinarily sufficient to accomplish this. As a rule steam agitation is to be preferred to air as the latter is apt to cause chemical changes in the cement, of the same character as described under

blown oils, and such changes are likely to produce a material lacking in uniformity unless its consistency is carefully watched and controlled by determinations made from time to time. If steam is employed, care should be taken to prevent its partial condensation before being forced through the mixture or otherwise the water carried along will cause the cement to foam badly. Any water present in the flux will have the same effect and it is, therefore, customary to specify that the flux must be free from water.

Mechanical agitation is sometimes resorted to and serves the same purpose as steam or air agitation, although perhaps not quite so effectively. Besides being necessary for a thorough mixing of flux and solid bitumen, agitation prevents local overheating to a great extent and, therefore, cracking and coking of the heavier hydrocarbons.

Sometimes blown oils are employed as fluxes for comparatively small amounts of the solid native bitumens. mixtures containing gilsonite have been quite extensively manufactured in the past few years and sold both for street paving and road work. The gilsonite is crushed fine and added directly to the flux while still in the converter. The flux is partially blown before the addition is made and is maintained at a temperature of about 205° C. After the gilsonite has been added, the blowing process is continued until the cement attains the desired consistency. Refined tars or tar residuums in conjunction with oil residuums have also been employed as fluxes for gilsonite in the preparation of road binders. The gilsonite cements are as a rule short and non-ductile, but possess a rubbery consistency quite different from the true asphalt cements. Blown oil gilsonite products have been sold under the name of mineral rubber and the pavements in which they have been employed are known as mineral rubber pavements. The characteristics of a typical blown oil gilsonite cement are given in the following table.

BLOWN OIL GILSONITE CEMENT.

| Character | ut sticky |
|---|-----------------|
| Specific gravity, 25°/25° C | 0.979 |
| Melting point, degrees C | 75° |
| Penetration 25° C., No. 2 N., 100 gms., 5 sec | 32° |
| Loss at 163° C., 5 hours | 0.57% |
| Character of residue somewh | at harder |
| Penetration of residue (as above) | 21 ⁰ |
| Soluble in CS ₂ , air temperature | 99.57% |
| Organic material insoluble | .29% |
| Inorganic material | .14% |
| | 100.00 |
| Per cent bitumen insoluble in 86° naphtha, air temp | 26.00% |
| Fixed carbon | 9.36% |

When tar is employed as a flux for gilsonite, it has been customary to first prepare a gilsonite oil cement of about the consistency of an ordinary asphalt cement and then to cut this product with a fluid tar residuum until the mixture has attained the consistency of a very viscous liquid. The properties of such a mixture prepared for use as a permanent road binder are given below.

GILSONITE OIL TAR PREPARATION.

| dissonting of the tremation. | |
|--|-------------|
| Specific gravity, 25°/25° C | 1.127 |
| CharacterViscou | ıs, sticky |
| Loss at 100° C., 5 hours | 1.35% |
| Loss at 163° C., 7 hours | 11.74% |
| Loss at 205° C., 7 hours | 19.36% |
| Character of residueCrack | ed, brittle |
| Distillation Test: | |
| Distillate to 110° C., per cent by volume | Trace |
| *Distillate 110° to 170° C., per cent by volume | 4.9% |
| †Distillate 170° to 240° C., per cent by volume | 26.3% |
| Pitch residue | 68.8% |
| | 100.0 |
| Soluble in CS ₂ , air temperature | 96.62 |
| Organic matter insoluble | 3.18 |
| Inorganic matter | . 20 |
| | 100.00 |
| Insoluble in CCl ₄ , air temperature | 8.61% |
| Insoluble in 90 per cent benzol, air temperature | 6.21 |

^{*} This distillate when cold held about one-twelfth its volume precipitated solids.

[†] This distillate when cold held only a very small amount of solids. It separated into two layers, one apparently an oil and the other a tar product.

An asphaltic cement for street paving should in most cases show a penetration at 25° C. of between 30 and 90. The desired consistency, as has been stated, is obtained by using the proper amount of flux. The proportion of solid bitumen to flux must of necessity vary with the character of both. extremely hard asphalt will ordinarily require more flux than a comparatively soft one and a greater amount of a dense residuum will be required than of a more fluid one in order to produce a cement of a given consistency. No definite rule can however be laid down in regard to this matter. The percentage of naphtha insoluble bitumen in a normal cement will usually lie between 20 and 35 per cent. For street paving work such properties as susceptibility to temperature changes, stability and ductility are important points to be considered. For road treatment much broader limits may be allowed, and while it may sometimes be desirable to employ a road binder having a penetration of 200 or less, good results may often be obtained by the use of viscous fluid bitumens originally too soft for a penetration determination, but which will in time attain a considerably harder consistency. Except when blown oil products are employed it is probably desirable that the cement show a higher penetration than in sheet asphalt work for the reason that in road work the binder is not depended upon to produce stability in the mineral aggregate, and the softer binders are not so apt to become brittle at low temperatures.

Summary and Conclusions. — In this chapter the physical and chemical characteristics of the semisolid and solid native bitumens have been considered with especial reference to their use as road binders. No attempt has been made to discuss their relative merits as applied to sheet asphalt pavements, other than to show the most important differences which exist between the two subjects. The asphalt pavement has been very exhaustively treated by Richardson to whose work * the reader is referred for further information along this line.

One of the most important facts which should be noted is

^{* &}quot;The Modern Asphalt Pavement," Wiley and Sons.

that binders totally unsuited for the construction of sheet asphalt surfaces may often have very desirable qualities for use as road binders. While the data accumulated in the paving industry relative to the characteristics of various solid bitumens and fluxes are well worthy of careful study, the standards so developed can by no means be considered a criterion for road work, and this is a point which should be remembered but which is often overlooked.

Nearly all of the bitumens described in this chapter are suitable or can be made suitable for various types of road work, but owing to cost it is doubtful if many of them will ever be extensively employed for this purpose. The domestic products such as the malthas, rock asphalts and gilsonite will of course be employed to some extent, especially in localities in which they occur. It is doubtful, however, if the more costly imported asphalts will be able to successfully compete with the cheaper artificial asphalts which are now produced in large quantities for road work and which if properly prepared should give excellent service.

CHAPTER X.

THE APPLICATION OF PETROLEUM AND ASPHALTIC MATERIALS.

In this country the first attempt to treat road surfaces with petroleum was made in Santa Barbara County, California, in 1804. Crude petroleum from the Summerland wells was sprinkled upon an earth road for the purpose of laying the dust. It proved very effective as a dust preventive, and being asphaltic in character improved the condition of the road surface to such an extent that popular attention was aroused, and, as a result, many experiments were commenced with a view not only to laying the dust but to bonding the surface as well. By 1898 the use of crude California oil for road treatment had spread through a number of counties, where it had come to be generally regarded as the solution of the dust problem, especially by fruit growers whose industry had long been injured by the damaging effect of road dust upon their produce. By 1800 the treatment of roads with both crude and residual oils had extended to a number of other states, and by 1902 experiments had been reported from Texas, Pennsylvania, New Jersey, Indiana, Colorado and the District of Columbia. By 1904 the field had broadened still further, but the work had all been of an experimental nature and the most varying results were reported. The only important fact that had been generally learned as to the relative value of different petroleums was that the paraffin oils had not proved satisfactory for road treatment and that those of an asphaltic nature were to be preferred. California, where work was naturally confined to this type of oil, good, bad and indifferent results had been obtained so far as improvement of the road surface was concerned, although from the standpoint of dust suppression the work had proved

very successful. Road engineers had begun to realize that in order to produce good results something more was necessary than to pour any kind of oil upon any kind of road surface. Oil sprinklers or wagons fitted with spreading devices had become quite common, and the use of the heavier crude and residual oils which required heating before they could be successfully applied, was regarded as best practice.

In 1905 the use of oil for road treatment advanced rapidly and during the last four years, owing to the very widespread interest in the problems of dust suppression and road preservation, the total mileage of oil treated roads has increased by leaps and bounds. Road oil industries have been developed for the purpose of producing and selling oils suitable for application in a variety of ways under varying conditions. These products have been used indiscriminately and the greatest variations in results have been reported. The whole subject is yet in an experimental stage and much is to be learned as to the effect of certain physical and chemical properties of an oil upon the results obtained in practice. Unfortunately the consumer while responsible for numerous experiments has as a rule neglected to make an examination of the oil he has employed, and this fact has to a great extent detracted from the value of his reports for others who wish to work along similar lines. While some attempts have been made to review these reports, the conclusions arrived at by this means are vague at best, and road engineers are often forced to learn by experience what should by this time be common knowledge.

California is particularly favored by nature for oil road work, as regards the character of her oils, her climate and her soil. Experimenters in other states have not as a rule realized the importance of this fact, and in attempting to duplicate California methods have met with failure because of different local conditions which require somewhat different treatment.

Application of Oils in General. — The subject of oil application, unlike that of tar, has received considerably more study in this country than has been given it by European nations. It



is true that various experiments have been carried on in England and France with a number of different oils, but owing to the lack of a proper base in these oils the results have been discouraging. Shale oils and Russian petroleum residuums, known as "masut" or "astatki," have been employed. They have all been found effective as temporary dust preventives, but in rainy weather produce a greasy, disagreeable mud and soon disappear from the road surface. The best results have so far been obtained with heavy oils applied in the form of a spray while hot.

Under favorable conditions oils may be applied to earth, gravel and broken stone roads with good results, and in any case application may be made either to the surface of an old road or to the body of the road during resurfacing or construction. In broken stone roads the roadstone may also be mixed with the oil before being laid, in which case the work more nearly resembles the city street form of construction. A number of distributing devices have been invented for the purpose of facilitating application, and special machinery has been designed for convenient handling and transportation of the oil as well as for incorporating it with the road material.

Surface Application of the Lighter Crude Oils. — An oil applied to the surface of a road will serve only as a temporary or semipermanent binder. Crude oils with the exception of those found in California should be considered mainly as dust preventives as they have little to recommend them as road binders. If sufficiently fluid they may be applied cold by means of an ordinary street sprinkler, but only in sufficient quantity to saturate the dust present on the road. A number of light applications during a dusty season is to be greatly preferred to a single heavy one, for the latter is apt to be incompletely absorbed by the road and will require sanding in order to take up all excess of oil. Even then the surface will become greasy and slippery unless the oil is very asphaltic in character. In addition the road will cut up badly under traffic in wet weather.

No set rule can be laid down as to the proper quantity to apply because of the variance in the capacity for absorption of different road surfaces. Earth roads will require more than gravel roads and gravel roads more than macadam. The consistency of the oil itself may often modify the amount required as the very fluid oils will be absorbed more readily than those which are non-viscous. The ideal treatment would be to use just sufficient oil at one application to lay the dust for a season and at the same time prevent the formation of an undesirable surface condition. This is of course a difficult matter to estimate, but for macadam roads will average from 0.3 to 0.6 gallons per square yard and for earth roads sometimes as high as 1.5 gallons and over per square yard. Gravel roads will require an intermediate amount. If containing a relatively large quantity of volatile oils the crude asphaltic petroleums may develop considerable binding power in the course of time under atmospheric conditions and, as has been stated, it was this property that first aroused public attention in California.

The cost of treating a road surface with crude oil can be only approximately estimated, as the value of the oil varies in different localities (see statistical tables, Chapter VIII), and the amount of oil required is an uncertain quantity. In general the method is not to be recommended unless the oil holds a truly asphaltic base and the dust can be successfully laid for not over three cents per square yard per season.

Application of Oil Emulsions. — Emulsions are applied to the road surface in much the same manner as the fluid crude oils, i.e., after dilution they are sprinkled upon the road by means of an ordinary street sprinkler. As it is necessary to dilute them before using a method similar to that described for calcium chloride (see page 49) by which they may first be distributed at the different hydrants along the road, is the one which is most apt to prove economical. The quality of the oil contained in the emulsion is of course a very important factor to be considered and only those holding a good asphaltic base should be used. Preparations of this sort are now found upon

the market or may be made by the road supervisor as described in the preceding chapter.

When employing the class of asphaltic oil emulsions now found upon the market it is customary to give the road either one treatment or else two, with a short interval between, of a 15 to 18 per cent solution. The surface is thus thoroughly impregnated with the asphaltic binder, and as the emulsifying agents are more or less volatile, an insoluble and almost waterproof deposit is finally formed upon drying. This binder is not easily removed by rains or traffic, and if weaker solutions containing about 5 per cent of the original emulsion are applied from time to time the dust will be well laid. At the end of a season the road should not only be in better condition than at the beginning, but its wearing quality should be more or less permanently improved, according to the amount of binder which has been retained. These emulsions can be purchased for about sixteen cents per gallon in concentrated form, and are usually contained in iron drums holding one hundred and twenty gallons each. In the first treatments one gallon of the original emulsion is applied to about every thirty square yards, and for succeeding treatments the same amount is made to cover from sixty to ninety square yards, according to the strength of solution employed. The total cost per square yard during an average season will run from four to six cents, according to locality and traffic conditions. While this is somewhat higher than the cost of treating with soap emulsions of oil, the results obtained are more permanent, and this fact should be taken into account when comparing the two. Up to the present time the oil emulsions have been used principally upon parkways and suburban roads, as the cost of frequent treatment precludes their use on rural highways.

When intelligently and systematically applied, the appearance of a macadam road so treated is at the end of a season much improved and for the depth of from one-quarter to one-half inch should show an accumulation of asphaltic oil which binds the surface stone together sufficiently to withstand the

ordinary disintegrating effect of winter weather. At the beginning of the next dusty season, however, the treatments should be renewed. The treatment of earth roads with emulsions is not to be advised because of the high cost resulting from the necessarily large quantity required. It is possible that satisfactory results may be obtained at a reasonable cost in the treatment of sand-clay, burnt-clay and gravel roads, but the macadam certainly offers the best field for this type of binder. Extremely heavy asphaltic oil emulsions which will quickly evaporate to the consistancy of a semisolid binder have been used to a limited extent, in the neighborhood of Chicago, in the construction of macadam roads. Roads so built have not, however, been down for a sufficiently long time to warrant any definite opinion as to their merits.

When soap emulsions are prepared according to the formula given in Chapter VIII, it is good practice to apply a 16 per cent solution at first and from 5 to 10 per cent solutions following, according to the needs of the road. The number of applications required during a season will vary with conditions. They are usually made, however, from ten to twenty-five days apart. By the use of a soap emulsion of this kind the loose material on the road is held down, but is not bound firmly together nor to the road surface. A thin rolling cushion is produced, saturated with oil, which prevents dust formation and protects the underlying surface. A very light coating of sand or fine stone screenings is sometimes spread on the road before applying the emulsion. This produces a surface which is hard and firm and will take a considerable amount of wear. The main objection to this thin rolling cushion is that under the action of traffic it is apt to be worked to the sides of the road and finally into the gutters. It is then necessary to throw the old material back or apply fresh material, and this of course requires constant attention and considerably increases the cost of the work. certain cases the cost of applying sufficient emulsion to lay the dust for a season has been as low as two cents per square yard, as compared with the cost of watering in previous seasons, of

three cents per square yard. The cost of applying sand and throwing back material which is carried to the gutters should, however, be added to this in order to obtain the actual cost of maintaining the road in proper condition. Except for a rather faint oily odor, no unpleasant results are obtained from an emulsion of this sort. The principal advantage is its cheapness, which is due to the fact that it is manufactured by the experimenter. It has been found that if too much is applied at one time an undesirable loose scale is formed when the surface dries out. This is undoubtedly due to the soap used, which to some extent destroys the true binding value of the asphaltic base, owing to the presence of fixed alkalies. Light applications at more frequent intervals are, therefore, to be preferred.

Surface Application of Heavy Crude and Refined Oils. - The heavy crude and rather viscous residual oils and cut back products require heating before they can be applied successfully to a road surface. Such materials, to be satisfactory, should serve as semipermanent binders, as the cost and trouble of applying them is too great for mere dust palliatives. They may be purchased by the barrel or by the tank car, the latter being cheaper and preferable from the standpoint of heating, provided the car is properly equipped with steam coils.

If much work of the kind is to be carried on in one locality, it is sometimes the custom to erect a stationary heating plant at a convenient railroad siding. A plant of this sort may consist of a receiving tank of one tank-car capacity placed preferably so that the oil may be run in by gravity from the car. A heating tank set at an elevation sufficient to allow the hot oil to run into the distributing wagons, and fitted with steam coils through which superheated steam may be forced, is placed near the receiving tank. The oil may be pumped into this heating tank as required and heated to any desired temperature. Very often the heating is carried on in the tank car, and the hot oil run directly into the distributing wagon. When sufficiently fluid, it can then be applied to the road by means of a large pipe and broomed into the surface. Patented distributing devices have been employed which can be attached to almost any form of tank wagon and which, if the oil is fluid enough, will do away with the necessity of brooming. An oil applied by this means will, however, have to be heated to a higher temperature than in the former case, as the openings in the distributer are of small dimensions and will not allow the oil to pass freely if it is in a very viscous state.

Oil Sprinklers. — Oil sprinkling carts equipped with compressed air chambers for the purpose of forcing the hot oil upon the road in a fine spray under pressure are now being used to some extent and are to be recommended, for by this means a uniform distribution can be secured and the quantity of oil applied per given area easily controlled. Such a machine is



Fig. 15. Saybolt High Pressure Road Oil Distributor.

shown in Fig. 15, and types of oil distributing devices which may be attached to the ordinary sprinkler in Figs. 16, 17 and 18.

Fig. 15 shows a lately devised high-pressure automatically propelled road oiler of an American make. This machine deserves

notice as being one of the first of its kind manufactured in the United States, although somewhat similar machines have been used in England and France for some time past and a few imported to this country. During the summer of 1909 it was tried out in practice in a number of the eastern states with considerable success.

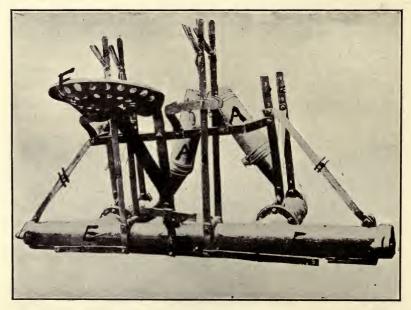


Fig. 16. Asphaltoilene Distributor.

In Fig. 16, AA represent the conveyors which carry the oil from the tank wagon to the distributor, and BBBB levers operating the four valves which control the flow of oil from the four sections of the distributor E, which is six feet wide. Each lever is provided with a ratchet and can be adjusted to deliver from one pint to two gallons to the square yard for a width of eighteen inches. The lever D serves as a foot rest for the operator, who sits in the seat F and operates a valve for rapid control of the entire flow. The distributor is attached to the sprinkling wagon by means of supports GGGG which are braced

by the attachments HH. Fig. 17 shows this distributor in operation.



Fig. 17. Asphaltoilene Distributor in Operation.

Fig. 18 shows another type of detachable distributor consisting of an equalizing tank or reservoir connected with the



Fig. 18. American Tar Company's Distributor.

distributing pipe and mounted on wheels. It may be readily attached to any kind of tank wagon fitted with an outlet pipe in the rear as there are no complicated connections, the distributor being simply trundled along behind the wagon. It is operated by means of a single lever and is so arranged that it distributes the material over the road surface to any width from six feet to six inches. Owing to the equalizing tank a uniform pressure is kept on the distributing nozzles independent of the amount of liquid in the tank wagon.

Measurement of Hot Oils. — When heating an oil for application it is advisable to raise its temperature only just high enough to allow to be easily handled and properly applied. The minimum temperature will necessarily vary with different oils according to their composition and original viscosity, but in no case should an oil or oil product be heated higher than 350° F. (177° C.). It is sometimes desirable to measure this oil while hot and for this purpose its volume at 60° F. (15.5° C.) is taken as normal and a deduction of 0.4 per cent is made for every 10° F. increase over the normal temperature, as a correction for expansion by heat. Thus if a tank wagon having a capacity of six hundred gallons is filled with oil at a temperature of 260° F. the actual amount of oil at 60° F. would be calculated as follows:

$$600 \div \left(\frac{260 - 60}{10} \times .004 + 1\right) = 555.5 \text{ gals.}$$

The general formulas for finding the volume of a hot oil at normal temperature, calculated by means of Fahrenheit and Centigrade degrees are given below, V being in both cases the volume while hot.

Volume at 60° F. =
$$\frac{V}{.0004 \, (^{\circ} \, \text{F.} - 60) + 1}$$
.
Volume at 15.5° C. = $\frac{V}{.00072 \, (^{\circ} \, \text{C.} - 15.5) + 1}$.

While this method of calculating the actual volume of oil is not theoretically correct, owing to the differences in coefficient of expansion of different oils, it is near enough for all practical purposes and is customarily used for asphaltic oils. It is, however, preferable to purchase oil by weight if it is delivered hot and the facilities for weighing it are at hand.

Surface Treatment of Earth Roads. - The surface treatment of earth roads with heavy oils is now almost a thing of the past, as it has been found far more satisfactory to harrow the oil into the body of the road and practically construct an oil-earth road. If a purely surface application is to be made with an asphaltic oil, the surface may be improved to some extent by the formation of a thin crust of oiled earth, which will, however, tend to break through and scale off. If a semiasphaltic oil is used, the surface will become mealy, and while the dust may be laid for some time, a disagreeable mud will be formed in wet weather. Before application the road should be shaped up with a drag or road machine, all loose places compacted and ruts well filled, as the oil tends to collect in the low places and unless well mixed with the earth will form soft spots. The surface should not be rolled to any extent as it is desirable to have about one-half inch of loose earth to absorb the oil. After application this cushion of oiled earth should compact sufficiently under traffic.

It has been found that the character of the soil plays a most important part in the results obtained, and different kinds of soils have to be treated in different ways. Alkali soils disintegrate the oil and destroy its binding qualities. A sandy loam is the most suitable for treatment, and almost invariably gives good results when treated in the proper manner with an oil of good binding quality. From a physical standpoint clay is probably the worst of all, as it does not absorb the oil well and exhibits a tendency to ball up and give trouble. Sand should therefore be added to the clayey surface until this difficulty is overcome. Special attention should be paid to drainage, and the roadbed should be dry when the oil is applied. If the foundation is water-soaked, it soon loses its ability to properly support the surface, which will then break through in weak

spots. The use of too much oil should be avoided, as it will produce a spongy surface condition and increase the draft of vehicles to a considerable extent.

. Surface Treatment of Gravel Roads. — Gravel roads are as a class better adapted to surface treatment with heavy oils than any other and in the eastern part of the United States have proven most satisfactory when the proper kind of oil has been employed. In fact a well compacted gravel road if built of a good cementing gravel requires but little additional binding material to lay the dust and put it in condition to successfully withstand automobile and light horse drawn traffic. application of even a temporary binder will sometimes produce surprisingly satisfactory results. The best gravel for treatment with oils is one containing just sufficient clayey material to act as a natural binder for the larger particles. It is impossible to state just the proper amount of clay as the proportion will vary for different gravels. Experiment alone will determine this but it will be found that too much clay is less desirable than too little.

It is very important in a gravel road that the drainage be good, and this matter should be attended to first of all. Any holes or pockets which may exist should be cleaned out, if much fine material is present, and filled with clean, fresh gravel, so that the surface of the road will be uniform when the patches have been sprinkled and rolled. If the lateral drainage is bad, the entire surface should be loosened and brought to proper grade and crown by the addition of new material before the oil is applied. In this case more oil will be required to produce a good bond than if the old compacted surface is treated, but the results will be of a more lasting character. The oil should contain a high percentage of good asphaltic base, or otherwise the material near the surface will become loose, owing to the lubricating qualities of the oil. The use of too much oil should be especially avoided, and all excess should be taken up by the addition of fresh gravel. Where the surface treated is loose and contains a considerable amount of clay, the oil may be worked into the

upper course by raking, which insures an equal distribution. After application of the oil, the road should be rolled until properly compacted, and as this is apt to bring some of the oil to the surface, fresh material should be added where necessary. If the freshly oiled road is not well rolled, the action of traffic will bring the oil upward; a soft spongy surface condition will be produced; loose, oily particles will be thrown out by rapidly moving vehicles; and the oil will be tracked by pedestrians.

Shell roads may be treated in the same manner as described for gravel roads.

Surface Treatment of Macadam Roads. — Before applying a semipermanent oil binder to a macadam surface, it is absolutely essential that the road be put in good repair, if satisfactory results are to be obtained. Failure to do this has resulted in many unsuccessful experiments which might otherwise have proved entirely satisfactory. No mere surface application will ever put a poor road in good condition, and the most that can be expected from an oil so applied is that it shall keep a good road in good condition for a reasonable length of time. Much of course depends upon the character of the oil, but the best cannot do more than this. Particular attention should be paid to drainage and all holes and depressions should be filled and the surface brought to even crown and grade, sometime in advance of treatment, in order that the repairs may become well consolidated by traffic. This is necessary because most oils intended for the surface treatment of old roads have not sufficient binding strength to hold down fresh patches. If applied to such places at the same rate as to the rest of the road they are apt to be entirely absorbed into the body of the road, and if in larger quantities to produce soft spots. When it is impracticable or inconvenient to make repairs in advance, the use of some heavier binder such as might be employed in construction work is to be advised in places where new stone is required.

Before applying the oil, much more dust may be allowed to remain upon the road surface without bad effect than in the case

of tars. There is a limit, however, which is often exceeded and this has been the cause of many failures in oil treated roads. It is safe to say that a very dusty road should always be swept before oiling, and if any doubt exists as to the advisability of sweeping the road, the behavior of the oil itself when applied upon a short section should serve as a guide. Other things being equal, heavy oils should produce more lasting results than light oils, but owing to their lower penetrating value, they cannot be satisfactorily applied to as dusty a surface as the latter. If, therefore, the oil tends to puddle without being absorbed by the road surface, the presence of too much dust is indicated. The remainder of the road should then be swept, after which a better absorption or penetration of the oil will be obtained. Under the conditions mentioned it is exceedingly bad practice to continue the application of oil to the dusty surface and rely upon a coat of sand or screenings to hold it in place, and yet this is often done. The application of too much oil is also a frequent cause of failure. All macadam surfaces will not require the same amount, and as no set rules can be laid down in this regard it is a matter for the exercise of some little judgment. Too often application is made by rule of thumb and a given quantity of oil, usually 0.5 gallon per square yard, is applied whether or no. In some instances 0.3 gallon is more than sufficient and in others 0.6 or 0.7 gallon per square yard should be applied, depending not only upon the condition of the road surface but upon the character of the oil itself.

The condition of the road surface with respect to its moisture contents at the time application is made often exerts a very marked influence upon the results obtained. This matter requires more study before any very definite assertions can be made, but it may be said that while an oil should never be applied in rainy weather or to an absolutely wet surface, a slight amount of moisture is preferable to an absolutely dry and powdery surface. Instances have come under the writer's notice where sections of the same road built of the same rock and apparently in the same condition, have produced somewhat

different results after treatment with the same oil as shown by analysis. The only rational explanation for these differences would seem to lie in the relative moisture contents of the surface at the time of treatment. Variations in the character of the roadstone will, of course, exert an effect upon the way an oil will incorporate with the road, as some rock powders produce a tough elastic mixture while others are crumbly when mixed with oil.

The main object in oiling a macadam road is to obtain an even coating, which shall be well absorbed by the road surface. The application of a large excess of oil is sure to make the surface sticky and disagreeable. A covering of sharp sand or one-half inch stone screenings should be applied after the oil has been allowed to penetrate as much as possible, in order to take up all excess, and the surface thus formed may then be rolled until well compacted, additional sand or screenings being thrown on wherever the oil shows a tendency to force its way to the surface and produce a sticky condition. Sometimes two or three courses of oil and screenings are applied. It is usually considered better practice to allow the freshly oiled road to dry out to some extent before applying the top dressing, but in cases where it is impossible to keep traffic away either one-half the width of the road may be treated at one time or the sand or screenings may be applied at once. If the oil is well absorbed it is not necessary to employ the roller, as ordinary traffic will consolidate the surface in the course of time.

The objections which have been urged against oiled macadam roads are that the oil has an unpleasant odor, that it is tracked onto pavements and into houses, that particles of the road surface thrown up by the wheels of moving vehicles are injurious to clothes, that rubber tires are injured, that a disagreeable mud is formed in wet weather ruinous to the varnish on vehicles, and that the tractive resistance of the road is increased. If the right kind of oil is applied under proper conditions most of these objections can be overcome. A good asphaltic residual oil should have but a faint odor and even

the odor of cut-back products should shortly disappear as the lighter constituents volatilize. Application of too much oil or the presence of too much fine material on the road surface are the most frequent causes of the remaining objections. In a finished oiled macadam the fine material should be just saturated and no more, and this can be controlled by sanding. If this is done the oil should not track and particles of the oiled road surface should not be more injurious to clothes than any other dirt. A proper mixture of oil and stone dust should leave no stain when placed upon a piece of cloth. The oil may of course be tracked shortly after being applied and while it is penetrating the road surface. At this time, as has been stated, the freshly oiled surface should be closed to traffic. So far as can be learned, an oiled road does not injure rubber tires unless a great excess of oil is present, so that this objection may be easily overcome. The presence of too much fine material upon the road surface is often responsible for the formation of a disagreeable mud in wet weather, and this together with the use of too much oil causes the increased tractive resistance often commented upon. If proper precautions are taken, however, and the right methods followed, an oiled macadam surface should be for the time being smooth, dustless, waterproof and resilient. It should have no disagreeable odor to speak of and its appearance should be pleasing and restful to the eyes, being of a seal brown color which does not produce the glary effect of an untreated macadam in bright sunlight. In dry weather it should show a crust of asphalt-like surface. Long continued rains and especially alternate freezing and thawing will in a short time destroy the bond of this crust to a great extent, and the treatment will ordinarily have to be repeated at the beginning of the next dusty season.

Construction of Oil Earth Roads. — Oiled earth roads have been most successfully constructed in California where, as has been stated, climatic conditions are favorable and the oil is best suited for such work. The methods originated and employed in this state are of great interest, and have been

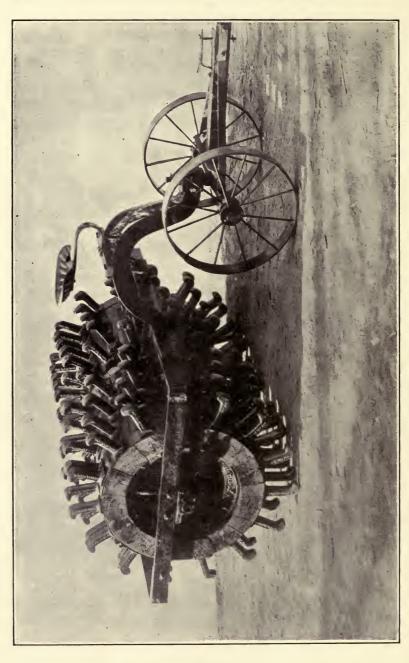
followed quite closely by experimenters in other sections of the country. In the earlier work such promising results followed the application of oil to earth road surfaces that attempts were soon made to further improve matters by incorporating the oil in the body of the road, with the hope of obtaining permanent results.

One of the simplest and cheapest methods of building such a road is to first cut it out to the desired cross section. The subgrade should be well compacted and all weak spots and holes filled with sound material and thoroughly consolidated. Oil may then be applied to this base at the rate of approximately one gallon per square yard, after which a road grader is employed to return the earth which has previously been removed to the sides of the road. While this is being done, a drag attached to the rear of the grader smooths the earth over the oil to a depth of four or five inches. The road is then thoroughly rolled and opened to traffic. The grader and drag should be used upon the road to smooth it up from time to time until the oil comes to the surface under the action of traffic. Such a method has been described by Eldridge * as producing good results.

Thorough incorporation of the oil with the earth is one of the most important factors to be considered in the construction of an oiled earth road, and if this is not accomplished an uneven surface will be produced which is soft and sticky in spots. A disk harrow and road grader are of great service in securing a uniform mixture, the harrow cutting up and pulverizing the clods of earth and the grader turning and rolling it from side to side. It has been found that the application of water to the roadway during process of construction is often a great aid in mixing as it keeps the earth in a finely divided state, thus allowing the oil to permeate the entire mass.

Another accessory for mixing and compacting the road which has been extensively used in California, is known as the rolling

^{*} Biennial Report, Department of Highways, State of California, December, 1906.



tamper. The construction of this machine, a type of which is shown in Fig. 19, was suggested by the effect produced by a large flock of sheep walking over a newly plowed road. After the sheep had passed it was noticed that the road had been packed extremely hard. It will be seen that the rolling tamper has the form of a roller, from the circumference of which project a large number of tampers which act like so many feet walking over the earth and packing it down. Owing to its peculiar construction this roller, under favorable conditions, consolidates the road from the bottom up, instead of from the top down as in the case of other rollers. The effect is much the same as would be produced by the flock of sheep passing over the road. For this reason it is sometimes called the sheepsfoot roller. As each of the tampers sinks into the road it compacts a small portion of soil beneath it, and as the head is larger than the shank, some dirt falls back into the hole formed when it is pulled out. In this way the earth is consolidated from the bottom up as the roller is passed back and forth, the roller eventually riding entirely upon the surface. This machine is better adapted for use on sandy or loamy soils than on clayey soils as the latter are apt to pick up and pack between the shanks of the roller until it fills up solid. A self cleaning device should overcome this difficulty to a great extent.

Another type of rolling tamper, quite similar to the above, which has been used in the east, consists of a series of cast iron toothed discs, loosely journaled upon an axle. The machine weighs about 5,000 pounds and each tooth has a surface area of about eight square inches. The weight upon each individual tooth as it passes over the road amounts to about 800 pounds, the pressure exerted being therefore about 100 pounds per square inch.

When employing a rolling tamper the following general method has been employed in constructing what is commonly known as a petrolithic earth road.

The road is first plowed up to a depth of six inches and properly crowned. All clods and lumps are thoroughly broken up by



FIG. 20. Petrolithic Spike Disc Harrow.

means of a harrow, preferably spike toothed, such as shown in Fig. 20, and the roadway well sprinkled with water. The tamping roller is then used to compact the loose earth from the bottom up, to the depth of two inches. After the under surface is made firm by this means, a heavy asphaltic oil is applied at the rate of from one to one and one-half gallons per square yard, and a cultivator passed over the road until the oil and earth are thoroughly mixed. The tamper is then used again and the road further compacted until only one and one-half inches of loose material remain on top. This is lightly harrowed and sufficient water added to moisten it. Oil is again applied, the surface rolled with the tamper until firm, and finally ironed down with an ordinary roller, additional application of earth being applied wherever necessary to take up any excess of oil. A road constructed in this manner will require from two to three gallons per square yard. Where the natural soil is very clayey it may be well to modify it by bringing in some sandy soil from the outside, if such can be obtained, and mixing the two together before applying the oil. An exceedingly sandy soil will on the other hand be benefited by the addition of a small amount of clayey material.

When an oil containing asphaltic hydrocarbons is applied to a road, it is probable that these products are selectively held by the finer products constituting the body of the road. In fractionating crude petroleum by capillary filtration, Day* has demonstrated the following facts.

- (1) "When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than at the bottom."
- (2) "When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffin hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom."

Similar results are undoubtedly produced under the action of traffic, especially in the case of oiled earth roads, and account for the rather rapid volatilization of light oils and also for the slimy surface condition of roads treated with oils containing considerable quantities of the less volatile paraffin hydrocarbons.

Roads constructed with earth and oil have not proven as entirely successful as was first expected even in the State of California, and at the present time it seems extremely doubtful if they will ever prove to be a satisfactory type of road in the eastern states when the above method is employed. In the first place for this sort of work it is quite necessary that the oil be capable of hardening after application to form a semisolid product which will increase the mechanical stability of the road and prevent rutting. California oils are the only natural oils which will do this, and the author knows of no residual or cut-back products produced outside of California which can be recommended for this purpose. Even the California oil when

^{* &}quot;The Production of Petroleum in 1907," U. S. Geological Survey, Department of the Interior, 1908.

incorporated in the body of the road to the depth of five or six inches requires a long time to harden, and because of this, much complaint has been made in regard to the great increase in tractive resistance of the road surface due to the presence of the oil. For the first year or so the road ruts badly and should be continually dragged and in some cases spiked up and turned over. After completion the road surface becomes softer, owing to the tendency of the oil to work upward under the action of traffic. In the course of time, however, a gradual hardening takes place and satisfactory results are eventually produced.

At the present time the cost of transporting California oil. to the eastern states is prohibitive for ordinary road work. some few cases, however, this has been done for the purpose of ascertaining whether or not the California work could be duplicated under existing conditions. The results obtained have apparently answered this question in the negative, for it has been found that climatic conditions make it almost an impossibility to keep the road in a passable state during the hardening process. This is particularly true in winter weather when owing to alternate freezing and thawing the road is churned up under the action of traffic into heavy oily mud to its entire depth, so that for a number of months in the year it is more or less a slough. Where the climate is similar to that of California, however, there seems to be no reason why as satisfactory results cannot be obtained as in that state, providing that California or similar oils are used.

If the oiled earth road is to prove successful in the eastern states, it is evident that a heavy semisolid or solid binder will have to be employed which immediately after application will produce the desired mechanical stability. In order to obtain a good mixture this would necessitate heating both the earth and bitumen and mixing them together before they are applied to the road. This would entail considerable expense and where rock is available would not be necessary, for a bituminous macadam could be constructed at a very slightly increased cost and in many respects would be preferable. In fact in Cali-

fornia the oil-earth road is undergoing a process of evolution leading to the use of broken stone in a type of road commonly known as the petrolithic macadam. This in itself is good evidence that even under the most favorable conditions the oilearth road has not been found altogether satisfactory. A description of this type of road will be given later.

Construction of Oil Gravel Roads. — Oil is applied to a gravel road during construction in a manner quite similar to the surface treatment already described, but certain points in regard to the method of construction should be noted. These facts are well presented by Eldridge in the report previously mentioned which contains specifications used in certain parts of California for the construction of oiled gravel streets. Certain portions of these specifications in condensed form are given below for the purpose of emphasizing the most essential points.

Before placing the gravel, the subsurface must be brought to grade and rolled with a roller weighing not less than two hundred and fifty pounds per inch width of tire. Upon this subsurface two layers of good gravel should be applied, the bottom layer having a thickness of five inches and the top a thickness of three inches after being rolled. The first layer should contain no stones larger than two and one-half inches in greatest diameter. The gravel must be uniformly spread on the roadway and well moistened, rammed one foot from the gutter or curb, and the remaining portion rolled with a roller of the type before specified. All depressions must be promptly filled, moistened and again rolled, the rolling being continued until the surface will not yield under the roller. On this surface the top layer of gravel, free from all stones larger than one inch in greater diameter, should be applied and compacted in the same manner as the first layer. Oil should then be evenly distributed over the entire surface at the rate of one-half gallon per square yard and covered with clean, sharp sand until no oil can be seen. After the lapse of not less than twelve hours, another application of oil should be made and sand distributed in the same manner and

the whole surface rolled until unyielding to the roller, as before described.

Construction of Petrolithic Macadam.—As has been stated, the petrolithic macadam is largely replacing the early petrolithic earth road in California. While various methods of construction are employed, they are all quite similar and the following description may be considered as typical of this class of road.

The roadbed after being graded and crowned is plowed to a depth of six inches and the soil thoroughly pulverized and cultivated as described under the construction of oil-earth roads. The road is then well sprinkled with water, after which oil is applied at the rate of from one-half to three-fourths gallon per square yard according to the depth of crushed stone which is afterwards to be used. The stone should run from two to four inches in depth and the quantity of oil used in the construction of the foundation should vary inversely with the amount of stone.

After the oil has been applied the road is thoroughly cultivated with the addition of water as needed. A second application of oil is then made at the same rate as the first and the road recultivated as before. A third application of oil follows this and the cultivation is again repeated until a thorough mixture of oil and earth has been obtained. Water is frequently sprinkled upon the road throughout this process and should finally produce an almost muddy condition. The road is then tamped with the rolling tamper, above described, until it is hard and solid, water being employed as often as necessary to keep the soil in the best condition for working. While the roadway is being consolidated the tamper should be continuously followed by a cultivator set so as not to disturb the sub-base already tamped. It is necessary that the cultivator be reset from time to time, the purpose being simply to prevent a too rapid consolidation of the road and assist the tamper in compacting from the bottom up.

After the roadway is hard and firm two to four inches of one

and one-half inch crushed rock is spread and cultivated into the top two inches of oiled earth, which should serve as a binder. A fourth coat of oil is then applied at the rate of from one-half gallon per square yard when two inches of stone are used to one gallon per square yard when four inches of stone are used. The oil and rock and oiled earth are then cultivated until thoroughly mixed, and tamped with the rolling tamper until hard and unyielding. At this point the surface while hard is quite rough with the marks of the tamper. A fifth application of oil is then applied at the rate of one-fourth gallon per square yard, and a coat of one-half inch stone screenings spread over the oiled surface. This course is sprinkled with water and rolled into the surface of the pavement with the rolling tamper. The whole road is then smoothed off with an ordinary roller.

In this work the top coat of screenings should not be oiled, as the oil below will be sufficient to saturate it under the action of the roller. It is important to thoroughly coat the large stone with oil and oiled earth so that the upper surface is absolutely homogeneous, and it is of course necessary to use a good grade of asphaltic oil. The heaviest oil which can be mixed in the manner described is to be preferred and it should be applied hot. The total quantity of oil required will run from about 2½ to 3 gallons per square yard depending upon the amount of stone used. In California it is claimed that such work can be done for approximately 90 cents per square yard when four inches of stone are applied.

Oil Asphalt Macadam Construction. — There are two methods commonly employed in the construction of oil asphalt macadam, known as the penetration method and the mixing method. These will be discussed in detail in Chapter XII under tar macadam construction, as the *modus operandi* is quite similar for both oils and tars. In brief the penetration method consists in first building an ordinary macadam road without the application of screenings to the top course. This course should, however, be thoroughly compacted with a roller, after which hot oil is applied at the rate of approximately one and

one-half gallons per square yard. The oil penetrates the road and should cover the stones to a depth of about two inches, after which a light coat of clean stone chips is applied in sufficient quantity to fill the surface voids after rolling. A seal coat of oil is then applied at the rate of approximately one-half gallon per square yard and enough screenings spread on to take up all excess of oil and form a dense smooth surface when rolled.

In the mixing method the upper course of stone is mixed with oil before being laid. The oil should invariably be heated and it is often desirable to heat the stone also. Mixing may be done by hand or machinery and the bitumen coated stone, while still warm, spread upon the road to a depth of from two to three inches. After rolling, a flush coat of oil is applied to the road surface, and the road finished with screenings as in the penetration method.

In oil macadam construction an oil product having considerable mechanical stability should be employed, and one approaching the consistency of an asphaltic cement, such as used in the binder course of an asphalt pavement, will produce the best results. In the penetration method such a material cannot well be applied as it will solidify upon coming in contact with the cold stone and, therefore, fail to penetrate the upper course to the desired extent. If this happens a heavy coat of sticky bitumen will remain upon the road surface which will have to be covered with a large amount of screenings. Under the action of traffic, the whole surface of bitumen and screenings is likely to pick up and peel off in patches. On the other hand, if too soft a bitumen is employed the road surface will be soft and wavy and will rut badly. Tractive resistance will be greatly increased and the oil will continually sweat to the surface under the action of traffic and the heat of the sun. Fluid residual oils are as a rule unsuited for this sort of work because they have no tendency to harden after application. The softer semisolid bitumens and cut-back products may, however, give satisfaction, if carefully applied.

In the mixing method it is possible to use an oil asphalt or asphaltic cement having sufficient original consistency to produce a firm solid road almost immediately after it has been applied. These points will be further discussed in the chapter on Selection. Both the penetration and the mixing methods may be employed when resurfacing old macadam roads, as will be described later.

Rock Asphalt Macadam. - In the construction of a rock asphalt macadam the subgrade is prepared in the same manner as for an ordinary macadam. All soft spots should be filled with sound material and the whole rolled until well compacted and solid. The lower course of broken stone should then be laid and rolled in the usual manner, enough screenings being applied to produce an unyielding surface. Upon this foundation should be spread a two and one-half inch course of crushed rock preferably ranging in size from one to two inches. This course should be rolled only sufficiently to produce a smooth even surface and no attempt made to reduce the voids in any other manner. Rock asphalt should then be thrown on from dumping boards by means of shovels and raked over the surface to a uniform depth of one-half inch. It should never be dumped directly upon the road from a wagon. After application it should be rolled into the upper course as thoroughly as possible, care being taken that loose earth and dirt are not brought upon the surface by the roller. A one-inch coat of the rock asphalt is next applied in the same manner as before and well rolled. Sometimes it may be advisable to apply the rock asphalt in a single one and one-half inch layer.

The roller should be kept moving back and forth parallel to the axis of the roadway and worked from the outer edge to the crown, as in ordinary macadam construction. If, in the last coat, the roller tends to pick up the rock asphalt, its wheels may be dusted with a light coating of cement or rubbed with a cloth saturated with kerosene. After rolling for some time the surface may begin to crack, if the weather is cool, in which case it is well to discontinue the rolling for a while and start again when the surface is warmer and more pliable. A tandem roller is better adapted for this sort of work than the ordinary three wheel road roller, although the latter is necessary for rolling the stone courses.

Best results can be obtained in warm dry weather and in no case should the temperature fall below 5° C. while the pavement is being laid. The broken stone of the wearing course should be clean and dry to facilitate adhesion, and of fairly uniform size so that enough voids will be present to allow the rock asphalt to be forced into the road. When first opened to traffic the cushion of rock asphalt is apt to rut, but finely irons out into a smooth firm surface not unlike that of a sheet asphalt pavement, provided the bitumen is of proper consistency and the sand aggregate fairly well graded. A product carrying from 7 to 10 per cent bitumen is best suited for this work. The percentage of bitumen should never fall below 6 per cent. While the wearing course may be composed of the rock asphalt alone, if the proportion and character of bitumen is just right and the sand aggregate well graded, it is preferable to have the upper course of stone take up the wear and tear of traffic and the rock asphalt simply fill the voids in the road and act as a binder for the larger stone. As traffic tends to force the material into the road even more than rolling, it is, however, advisable to leave a thin cushion coat of the material on the surface just after completion.

Rock asphalt may be employed in the resurfacing of old macadam roads in much the same manner as described for the construction of new roads. In this case the old macadam should first be spiked up, all holes and depressions filled and the road brought to proper crown, after which a course of clean crushed rock is laid and compacted as described for the wearing course in construction work. Application of the rock asphalt is then made and the surface finished as above described. If the road cannot be closed to traffic during resurfacing, it will be necessary to apply the rock asphalt to one side at a time, in which case, in order to avoid an unsightly joint along the middle

of the road, the point of over-lapping should not be rolled until last. Care must be taken that no dust or other extraneous material finds its way into this joint or otherwise the two sides will not bond together upon rolling.

When natural rock asphalt is close at hand the cost of constructing a rock asphalt macadam is but little more than ordinary macadam work in that locality. If the material has to be shipped for any considerable distance, however, it does not make an economical binder, as the freight on the 90 to 93 per cent of sand which it contains raises the cost out of proportion to the results obtained, as compared with other binders. If it is desired to build this type of road in such localities it will be found cheaper to obtain a local sand and mix it hot with a soft asphaltic cement in suitable proportions. This mixture may be used in exactly the same manner as the natural rock asphalt, and has the advantage of being absolutely uniform and subject to control by the road engineer. For the preparation of such a material recourse should be had to a mechanical mixer of the type used in the preparation of an ordinary asphalt surface mixture. It may be mixed by hand if preferred, but this will cost more in the long run than mechanical mixing if any considerable amount of work is to be done.

Summary and Conclusions.—In this chapter the surface treatment and construction of earth gravel and broken stone roads with oil and oil products have been described in some detail. In comparing the various types of oiled roads it may be said that in general the oil asphalt macadam constructed according to the mixing method will in the long run prove the most satisfactory and economical. Such roads should not cost at the outside over 20 to 25 cents per square yard in excess of ordinary macadam, and 15 cents may often cover this additional cost. The other types of road have their field of usefulness, however, and may in some instances be even preferable to the asphalt macadam. Surface applications of a good binding oil will invariably prolong the life of a road, and even the asphalt macadam will be greatly benefited by such treatments made

from time to time as occasion requires. All kinds of properly oiled roads are practically noiseless, waterproof and resilient and for the time being, dustless. In the course of time dust will, of course, accumulate on the surface and additional light applications of oil may then be required. Automobile traffic will cause far less damage to an oil treated road than to the same untreated road. There are two enemies, however, that will have to be assiduously guarded against. These are water and frost action. No matter how carefully the oil has been selected and applied, failure will invariably result if the road is not properly drained both at the surface and foundation.

In conclusion mention may be made of one use of oil which, while not directly bearing upon road preservation, is closely associated with it. This is the application of a thin cushion of oiled earth to the plank flooring of bridges. Such treatment will be found to materially prolong the life of the wood beneath, which is thus protected from the wear and tear of steel shod traffic. For this purpose a heavy oil which will bind the earth particles firmly together and form a rubbery cushion is to be preferred.

CHAPTER XI.

TAR AND TAR PRODUCTS.

WHILE the term tar is applied to distillates produced in the destructive distillation of various organic materials, as stated in Chapter VII, it is only those produced from coal and petroleum that are of particular interest in the treatment of roads. Coal tars may be divided into three classes known as (1) gas house tars, (2) coke oven tars and (3) blast furnace tars, of which the first two are of the most common occurrence and by far the most important. Blast furnace tars are not at present a factor in road treatment and need not be considered. Petroleum tars may be classified as (1) water gas tars, and (2) true oil gas tars, according to their method of manufacture. As in the case of oils, considerable variations exist in both the chemical and the physical properties of tars, although here the differences are more directly related to the process of manufacture than to the locality in which they are produced. properties of the material distilled however exert considerable influence upon the character of tar.

The total production of coal tar and petroleum tar in the United States during 1908 amounted to 110,430,663 gallons valued at \$2,766,700. This is about 80,000,000 gallons less than that produced in the United Kingdom during 1906 from coal alone. The amount of coal coked and the tar produced therefrom in the United States during the years 1903 to 1908 are given in the following table.

COAL COKED AND TAR PRODUCED IN THE UNITED STATES.

| Year. | Coal Coked, Short Tons. | Tar Produced and Sold, Gallons. |
|---|--------------------------------------|--|
| 1903. 1904. 1905. 1907. 1908. | 7,058,157 8,187,812 11,490,661 | 62,964,393 69,498,085 80,022,043 103,577,760 101,261,829 |

The notable decrease for 1908 as compared with 1907 was due to the prevailing business depression, which materially curtailed the demand for coke. Had conditions been normal an increase in production would undoubtedly have been shown and it is to be expected that the statistics for 1909 will show a decided increase. The above table represents the report of some 471 producers.

The following tables, compiled by Parker,* show the production and value of coal tar and water gas and oil tars for 1907 and 1908 by states.

The chemical and physical characteristics of tars relative to their use as dust preventives and road binders require fully as much study as do the oils. As shown by the foregoing tables, this class of materials offers a very large source of supply and in the author's opinion a very valuable one. The value of tar for street paving work has been much belittled by those interested in the asphalt industry and because of their activities it has fallen into general disrepute, so much so as to be considered one of the worst of all adulterants. As a result of this it will undoubtedly take some time for tars to assume their rightful position in the eyes of the public, but the recent development of the bituminous road material industries, in which they are an important factor, is gradually accomplishing this result. (Had tars received as much study as oils and asphalts from the standpoint of paving, they would have been on a better footing long before now.) The methods of tar manufacture and a consideration of the characteristics possessed by different kinds of tars and their various constituents cover an immense field and volumes have been written upon only small portions of the subject. It is evidently impossible, therefore, in a single chapter to give more than a brief outline of the subject and point out in a general way the relations between certain properties of the materials and the results obtained by their use as dust preventives and road binders.

^{* &}quot;Mineral Resources of the United States, Calendar Year 1908." U. S. Geotogical Survey.

RANK OF STATES IN COAL TAR PRODUCTION IN 1907 AND 1908. 1907.

| Rank. | State. | Number of Establishments. | Quantity. | Value. | Value per Gallon. | Yield per Ton of Coal. |
|--------|------------------------------|---------------------------|-------------|-----------|-------------------------|------------------------------|
| - | | | Gallons. | | Cents. | Gallons |
| I | Pennsylvania | 28 | 18,304,661 | \$412,127 | 2.3 | 6.34 |
| 2 | New York | 50 | 13,769,436 | 302,290 | 2.2 | 9.58 |
| 3 | Massachusetts | 41 | 10,659,792 | 299,219 | 2.8 | 10.72 |
| 4 | Ohio | 32 | 8,095,305 | 218,986 | 2.7 | 11.23 |
| 5 | Michigan | 44 | 8,038,584 | 173,599 | 2.2 | 10.86 |
| 6 | Illinois | 40 | 6,383,125 | 125,049 | 2.0 | 8.49 |
| 7 | Alabama | 11 | 5,898,064 | 177,879 | 3.0 | 8.31 |
| 7 8 | Wisconsin | 21 | 5,436,098 | 129,556 | 2.4 | 7.70 |
| 9 | Delaware, District of Colum- | | | | | ' ' |
| | bia, and Maryland | 10 | 4,208,105 | 86,445 | 2.1 | 8.12 |
| 10 | New Jersey | 15 | 3,973,251 | 121,049 | 3.1 | 9.40 |
| II | Missouri | 14 | 3,870,388 | 90,452 | 2.3 | 19.63 |
| 12 | Virginia and West Virginia | 16 | 3,094,593 | 93,558 | 3.0 | 16.95 |
| 13 | Minnesota | 8 | 2,388,283 | 70,082 | 2.9 | 11.88 |
| 14 | Indiana | 29 | 1,498,434 | 36,049 | 2.4 | 10.71 |
| 15 | Kentucky | II | 976,622 | 22,577 | 2.3 | 9.98 |
| 16 | Connecticut | 7 | 886,359 | 32,114 | 3.6 | 12.09 |
| 17 | Colorado | 7 | 861,799 | 40,700 | 4.7 | 11.62 |
| 18 | Iowa | 18 | 759,317 | 18,906 | 2.5 | 10.98 |
| 19 | Tennessee | 7 | 754,135 | 27,233 | 3.6 | 11.31 |
| 20 | Rhode Island | 3 8 | 644,026 | 17,536 | 2.7 | 11.33 |
| 21 | Georgia | | 635,889 | 18,738 | 2.9 | 9.48 |
| 22 | Washington | 9 | 634,491 | 44,804 | 7.1 | 10.91 |
| 23 | Maine | 7 | 295,034 | 11,349 | 3.8 | 14.54 |
| 24 | North Carolina and South | | | | | |
| | Carolina | 7 | 291,871 | 11,792 | 4.0 | 10.53 |
| 25 | New Hampshire and Vermont | 5 | 235,324 | 11,388 | 4.8 | 11.94 |
| 26 | Texas | 7 | 225,394 | 12,707 | 5.6 | 7.97 |
| 27 | Oklahoma | 5 | 193,531 | 14,275 | 7 · 4 | 8.56 |
| 28 | Idaho, Montana, North Da- | | | | | |
| | kota, and Wyoming | 6 | 144,411 | 9,831 | 6.8 | 9.93 |
| 29 | Nevada, New Mexico, and | | | | | |
| | Utah Kansas and Nebraska | 4 | 120,925 | 7,431 | 6. I | 10.25 |
| 30 | Kansas and Nebraska | 5 | 113,522 | 4,082 | 3.6 | 7.99 |
| 3 r | Florida, Louisiana, and Mis- | _ | 0 7 9 | | | 6 |
| 20 | sissippi | 7 | 95,870 | 3,955 | 4. I | 10.60 |
| 32 | Arkansas | 3 | 71,700 | 3,771 | 5.3 | 11.38 |
| 33 | Oregon | 3 | 19,421 | 1,998 | 10.3 | 13.17 |
| | | 488 | 103,577,760 | 2 65x 505 | 2.6 | 0.01 |
| | | 400 | 103,5//,/00 | 2,651,527 | 2.6 | 9.04 |
| | | ! | | | | |

RANK OF STATES IN COAL TAR PRODUCTION IN 1908.

| | | Num- | | | | |
|-------|------------------------------|--------|-------------|-----------|---------|----------|
| | | ber of | | | Value | Yield |
| | Ct-t- | 1 | 0 | Value. | | |
| - 24 | State. | Estab- | Quantity. | value. | per | per Ton |
| Rank. | | lish- | | | Gallon. | of Coal. |
| × | | ments. | | | | |
| | | | | | | |
| I | Pennsylvania | 25 | 18,720,845 | \$401,052 | 2.I | 10.76 |
| 2 | New York | 48 | 14,688,079 | 315,664 | 2.1 | 10.33 |
| 3 | Massachusetts | 38 | 10,493,400 | 284,664 | 2.7 | 10.65 |
| 4 | Michigan | 42 | 7,834,757 | 182,571 | 2.3 | 11.45 |
| | Ohio | 27 | 6,774,193 | 192,682 | 2.8 | 12.32 |
| 5 | Illinois | , , | 6,248,695 | 140,199 | 2.2 | 8.13 |
| | Alabama | 45 | | 176,854 | 2.8 | 8.62 |
| 7 | | 11 | 6,244,491 | | | 8.01 |
| | Wisconsin | 10 | 5,557,537 | 135,311 | 2.4 | 0.01 |
| 9 | Delaware, District of Colum- | | | | | |
| | bia, and Maryland | 11 | 4,129,124 | 91,804 | 2.2 | 9.27 |
| 10 | New Jersey | 13 | 4,127,126 | 123,662 | 3.0 | 9.52 |
| 11 | Missouri | 15 | 3,874,454 | 89,403 | 2.3 | 21.60 |
| 12 | Minnesota | | 2,391,667 | 61,677 | 2.6 | 11.88 |
| 13 | Indiana | 30 | 1,587,817 | 40,395 | 2.5 | 10.76 |
| 14 | Kentucky | II | 1,397,492 | 29,676 | 2.I | 13.39 |
| 15 | Colorado | 6 | 926,094 | 42,621 | 4.6 | 9.92 |
| 16 | Virginia and West Virginia | 15 | 924,805 | 24,503 | 2.6 | 10.92 |
| 17 | Connecticut | 6 | 819,317 | 29,011 | 3.5 | 10.62 |
| 18 | Washington | 9 | 668,005 | 36,295 | 5.4 | 10.14 |
| 19 | Iowa | 16 | 658,454 | 18,444 | 2.8 | 8.82 |
| 20 | Tennessee | 7 | 646,760 | 24,422 | 3.8 | 9.43 |
| 21 | Rhode Island | 3 | 628,968 | 16,843 | 2.7 | 11.85 |
| 22 | Georgia | 9 | 299,424 | 11,021 | 3.7 | 4.14 |
| 23 | Maine | 7 | 278,105 | 10,120 | 3.6 | 13.36 |
| 24 | New Mexico, Oklahoma, and | | | | | |
| | Utah | 6 | 264,200 | 7,731 | 2.9 | 10.29 |
| 25 | North Carolina and South | | , | ,,,, | | |
| ŭ | Carolina | 8 | 253,520 | 10,467 | 4.1 | 8.56 |
| 26 | New Hampshire and Vermont | 6 | 238,847 | 12,076 | 5.0 | 10.78 |
| 27 | Kansas and Nebraska | 6 | 202,384 | 5,617 | 2.8 | 15.03 |
| 28 | Idaho, Montana, North Da- | | ,,, | J. 1 | | 0 |
| | kota, South Dakota, and | | | | | |
| | Wyoming | 7 | 128,170 | 8,455 | 6.6 | 8.49 |
| 29 | Texas | 6 | 101,580 | 5,788 | 5.7 | 4.63 |
| 30 | Florida, Louisiana, and Mis- | | | 3,1 | 3.7 | 73 |
| 3- | sissippi | 6 | 79,110 | 4,244 | 5.4 | 8.74 |
| 31 | Arkansas | 3 | 65,200 | 2,926 | 4.5 | 11.01 |
| 32 | California and Oregon | 3 | 9,200 | 920 | 10.0 | 5.41 |
| 32 | Camorina and Oregon | 3 | 9,200 | 920 | 10.0 | 3.41 |
| | | 471 | 101,261,829 | 2 527 178 | 2.5 | 10.30 |
| | | 471 | 101,201,029 | 2,33/,110 | 2.5 | 10.30 |
| | | 1 | | | 1 | 1 |

QUANTITY AND VALUE OF TAR PRODUCED AND SOLD AT WATER GAS AND OIL GAS WORKS IN THE UNITED STATES IN 1907 AND 1908.

1907.

| State. Quantity. Value. C | | | | |
|---|---|--|--|---|
| Arkansas, Florida, Louisiana, and Mississippi. 440,563 \$13,396 California and Washington. 3,388,891 78,554 Connecticut and Massachusetts. 2,142,476 58,914 Delaware, Maryland, and New Jersey. 1,871,500 45,850 Georgia and South Carolina. 34,439 2,262 Illinois, Indiana, and Ohio. 132,330 2,675 Iowa. 204,182 7,031 Minnesota and Wisconsin 664,457 21,699 Nebraska and South Dakota 454,314 11,205 Missouri. 3,050 163 New Hampshire 58,120 777 New York 3,619,788 72,626 Pennsylvania 1,207,156 24,152 | Price per Gallon. | | | State. |
| 14,414,017 342,041 | Cents 3.0 2.3 2.7 2.4 6.6 2.0 2.4 3.2 2.4 5.3 1.3 2.0 2.7 | 78,554 58,914 45,850 2,262 2,675 7,031 21,699 11,205 163 777 72,626 24,152 2,737 | 440,563 3,388,891 2,142,476 1,871,500 34,439 132,300 294,182 664,457 454,314 3,050 58,120 3,619,788 1,207,156 102,781 | California and Washington Connecticut and Massachusetts Delaware, Maryland, and New Jersey Georgia and South Carolina Illinois, Indiana, and Ohio Iowa Minnesota and Wisconsin Nebraska and South Dakota Missouri New Hampshire New York Pennsylvania |

1908.

| 2 14 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 | 1 | | |
|---|------------|---------|-----|
| California and Washington | | 35,471 | 4.9 |
| Connecticut, Massachusetts, and New Hampshire | 2,364,190 | 58,540 | 2.5 |
| Delaware and Maryland | 137,917 | 2,072 | 1.5 |
| Florida, Louisiana, Mississippi, and Texas | 558,714 | 15,207 | 2.7 |
| Georgia and South Carolina | 22,800 | 1,061 | 4.7 |
| Illinois | 21,600 | 524 | 2.4 |
| Indiana and Ohio | 557,322 | 12,360 | 2.2 |
| Iowa | 361,760 | 7,505 | 2.1 |
| Michigan, Minnesota, and Wisconsin | 615,055 | 19,316 | 3.1 |
| Missouri, Nebraska, and South Dakota | 458,637 | 10,357 | 2.3 |
| New Jersey | 114,900 | 1,805 | 1.6 |
| New York | 2,894,727 | 58,620 | 2.0 |
| Pennsylvania | | 6,744 | 2.0 |
| | | | |
| | *9,168,834 | 229,582 | 2.5 |

^{*} In addition 5,559,199 gallons were reported as produced but not sold.

Gas House Coal Tars. — Gas house coal tar is a by-product obtained in the manufacture of illuminating gas from coal. In the early days of manufacture it was considered a waste product having no value, and often proved a great nuisance to gas producers, who were at a loss to know how to dispose of it in a sanitary manner. Because of the great number of hydrocarbons which it contains it offered an inexhaustible field of research to many chemists and as a result of their investigations, great industries have sprung into existence whose basis of operation lies in the synthetic preparation of many valuable products hitherto unknown, or obtainable only at great expense from a few natural sources.

In the manufacture of illuminating gas, bituminous coal is placed in \square shaped fire clay retorts about 8 feet long, 15 inches high and 18 inches wide. Six or eight of these retorts are set together in a furnace and constitute what is commonly known as a bench. A number of these benches built together is called a stack. The retorts are usually set horizontally or at just sufficient angle to allow of their being discharged easily, and are heated by means of a coke fire or by generator gas. Fig. 21 shows the most important parts of the process in detail.

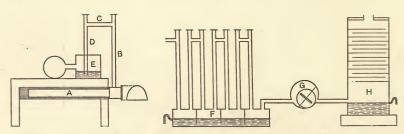


Fig. 21. Sketch Illustrating the Production of Tar in the Manufacture of Coal Gas.

Before the coal is heated all of the openings in each retort A are closed with the exception of a vertical pipe extending upwards from the front. The volatile products from the heated coal pass up this stand-pipe B which connects with the bridge C and the dip pipe D and are thus conducted to a long covered

trough running the whole length of the stack and known as the hydraulic main E, in which the greater part of the tarry products condense and collect under water, which is kept in the main to act as a seal and also to dissolve the ammonium salts which are formed. As the tar collects it is drawn off by various ingenious devices upon reaching a certain height in the hydraulic main. The gas now passes from the main to the condensing plant F, which usually consists of a series of vertical cast iron pipes connected at the top and opening at the bottom into an iron box which is divided by transverse partitions, extending nearly to the bottom and dipping into the condensed products so that the gas is forced to pass through the pipes. The condenser is cooled either by air or water in such a manner that the gas is brought slowly to a temperature of about 50°C. Tar and ammoniacal liquor are condensed here and flow from the box into a storage well. A mechanical device known as the exhauster G draws the gas from the condenser and forces it through the remaining parts of the plant. From the exhauster the gas passes into a tower fitted with numerous horizontal perforated plates called the tar extractor H, where the friction of the gas in passing through the perforations removes the last traces of tar. From this point on the process of gas manufacture ceases to be of interest in relation to the production of tar and it is only necessary to add that before the gas can be used for illuminating purposes it has to be further purified by passing it through scrubbers, washers and purifiers of different kinds in order to remove the remaining ammonia, carbon dioxide, hydrogen sulphide and other sulphur compounds formed. The nonvolatile part of the coal remains in the retort as coke. tar from the hydraulic main is thicker than that obtained from the condensers and scrubbers and poorer in volatile products. It represents about 62 per cent of the entire amount, while that from the condensers amounts to nearly 12 per cent and that from the scrubbers about 26 per cent. All of the tar is run together into large wells, where it is allowed to settle for some time in order to separate it as far as possible from the ammoniacal liquor present. This ammoniacal liquor being lighter than the tar rises to the top and is drawn off for use in the manufacture of ammonia.

The crude coal tar which remains is a black more or less viscid fluid of peculiar smell and varying in specific gravity from 1.10 to 1.25 and sometimes higher. As has been stated, it is an exceedingly complex mixture of chemical compounds and always contains a certain amount of ammoniacal liquor as well as several constituents of the illuminating gas in solution.

While the character of the coal will have considerable effect upon that of the tar produced, the temperature at which the retort is fired is also a most important modifying factor, as will be shown later. The temperature of the retort varies in different gas works from between 850° and 970° C., known as low temperature, to between 1100° and 1540° C., known as high temperature. From 970° to 1100° C. is considered medium temperature. The temperature of the coal is somewhat lower than that of the retort, especially at the center of the charge. The yield of tar per ton of coal will vary from about 8 gallons when high temperatures are employed to as much as 16 gallons at medium and low temperatures. The maximum variation as shown by the tables of coal tar production is from 4.1 gallons to 21.6 gallons. Other things being equal, the amount of gas produced increases with the temperature. In gas plants an attempt is made to get as much gas as possible out of the coal and, therefore, to distill at the highest possible temperature. Up to a certain point, this is quite rational, but beyond it modifying factors have to be considered. While the quantity of gas increases with the temperature, its illuminating power diminishes. This is due to the tendency displayed by the hydrocarbons to dissociate at high temperatures into their elements, hydrogen and carbon. Thus hydrogen will be produced as a gas and free carbon will be deposited in the tarry condensations, also the proportion of such substances as naphthalene and anthracene will be increased in the tar. If the higher temperatures are employed it will become necessary to enrich

the gas by the addition of oil products in order to give it the proper illuminating value. In cases where the enriching oil is cheap, the method is often employed, while in others it is considered more economical to produce a smaller amount of gas from the coal, which shall be richer in illuminants. The results of the examination of two crude coal tars, one produced at medium and the other at high temperature, are given in the following table:

CRUDE GAS HOUSE TARS.

| · | | | | |
|---|------------------------------|----------------------------|--|--|
| Туре | (1) Medium Temperature | (2) High Temperature | | |
| Character | Viscous, Fairly smooth | Viscous, Lumpy | | |
| Specific gravity, 25°/25° C | 1.188 | 1.250 | | |
| Distillation | 0.3 | 4.0 | | |
| First light oils to 110° C., per cent by vol | 4.4 | 2.5 | | |
| Second light oils 110°-170° C., per cent by vol | 16.5 | 17.5 | | |
| Heavy oils 170°-270° C., per cent by vol | 33.5 | 17.0 | | |
| Pitch residue (by difference), per cent by vol | 45.3 | 59.0 | | |
| • | 100.0 | 100.0 | | |
| Pitch residue, per cent by weight | 55 · 7 | 67.1 | | |
| Free carbon (insoluble in CS ₂) | 20.89 | 30.90 | | |
| | | | | |

Remarks. — In tar No. I the second light oil distillate showed about two-thirds of its volume precipitated naphthalene when cold, and the heavy oil distillate about two-fifths of its volume precipitated naphthalene. In tar No. 2 both the second light and heavy oils were nearly solid naphthalene when cold. The pitch residue of No. I showed a fairly lustrous fracture, while the fracture of No. 2 was dull.

A comparison of these two tars shows the effect of high temperatures in an increase in specific gravity directly attributable to the increase in free carbon, an increase in pitch residue, and a decrease in the heavy or dead oils. The presence of ammoniacal water and oils distilling below 110° C. is the distinguishing feature of all crude coal tars. Any amount of the former makes the tar unsatisfactory for road purposes, both because of the saponifying action of the ammonia and because water prevents proper absorption by and adhesion to the road

material. Tar No. 1 runs exceptionally low in this constituent and probably represents a sample which has been taken from near the bottom of the well after settling for a long time. It might be employed to some advantage in the surface treatment of a macadam road as a dust preventive and semipermanent binder, but would have to be applied hot. Tar No. 2 is in its natural condition unsuited for road work both because of the presence of water and its high naphthalene and free carbon content. As will appear later, neither tar is capable of being refined to make a good road binder unless blended with another tar having quite different characteristies. While crude tars are quite viscous, they sweat badly under the action of sun and traffic after being applied to the road, and have not sufficient body to be employed in construction work. The lumpy appearance of No. 2 is due to the presence of an excess of free carbon, which gives the bitumen a false consistency. The light oils can only be considered as volatile diluents, of no value for road purposes, although from the tar refiner's point of view they may be the most valuable constituent. The heavy oils are of service in keeping the tar from becoming too brittle after the lighter oils have evaporated, providing that they are not composed mainly of naphthalene, as in the case of No. 2. The true binding base of the tar is present in the pitch residue, although in order that it may be developed properly, it is necessary for it to be fluxed with heavy oils. While No. 2 has apparently a much greater per cent of this binding base than No. 1, as shown by the relative amount of pitch residue, it should be remembered that these residues contain free carbon which, as will be shown later, has no binding value. If the percentage of free carbon be subtracted in each case from the per cent of pitch by weight, it will be seen that there is very little difference between the two tars in the actual amount of bitumen present in the residues. Thus No. 1 would show 34.81 per cent and No. 2, 36.20, giving a difference of less than 2 per cent. While this would seem to be a slight advantage in favor of No. 2, it is not in reality, because of the proportionately small amount and inferior character of the heavy oils which are necessary to keep life in the tar.

Coke Oven Tars. — While in the manufacture of coal gas the production of tar is absolutely unavoidable, this is not true of the manufacture of coke for metallurgical purposes. There are two general types of coke ovens in use at present, in one of which no attempt is made to recover the volatile products of the coal. This is the oldest form of oven, known as "the beehive," and is extensively used in this country to-day. It is constructed of brick and as its name implies has the form of a beehive. Bituminous coal is placed in this oven or kiln and a part of it burned in order to carbonize the remainder, while the volatile products, such as gas, ammonia, and tar, are allowed to escape through an opening in the top of the kiln where they are lost in flame and smoke.

Coke ovens in which the by-products are saved are now used to some extent in this country and sooner or later will undoubtedly replace the old style oven entirely, and thus enormously increase our output of tar. The reason that they have not been more generally adopted in this country is that in the United States tars are of much less economic importance than in the European countries, where great chemical industries are based upon the utilization of this material. Germany in particular is far in advance of us in this field and exports to this country alone coal tar products to the value of several million dollars each year. With the development of the road tar industry, which promises to consume vast quantities of tar, and the necessity for refining such tars before use, the general adoption of by-product ovens is only a matter of time. What this will mean in the increase in tar production can be imagined from the fact that in 1908, out of a total of over 26 million tons of coke produced in coke ovens, only a little over 4 million tons were obtained from by-product ovens. About 22 million tons of coke were, therefore, produced without recovery of the tar. As the average yield of coke per ton of coal was 66 per cent, this would represent the consumption of over 33 million tons of

coal. Upon the basis of a yield of 10 gallons of tar per ton of coal, it may be seen that over 330 million gallons of tar were lost which might have been saved in 1908. As the actual production of coal tar both from coke ovens and gas houses amounted to about 101 million gallons, it is evident that over three-fourths of our possible production of tar as a by-product was lost during that year. At a valuation of two and one-half cents per gallon, this means a loss of over 8 million dollars. With such an increase in production, however, the monetary value of coal tar would have dropped, so that this figure may be somewhat exaggerated. In any event at a conservative estimate the tar lost each year from non-recovery coke ovens is sufficient to build 9,000 miles of tar macadam road, 15 feet wide.

There are several kinds of by-product coke ovens now in use, the most common being the Coppee, the Otto-Hoffmann, the Simon-Carves and the Semet-Solvay. In these a coke suitable for metallurgical purposes is produced, and the ammonia and coal tar recovered. Whichever oven is employed the method is entirely analogous to gas manufacture, and stripped of all details is conducted as follows: The coal is charged into long, narrow chambers or retorts of from 4 to 6 tons capacity, heated by means of flues set in the retort walls. The volatile portions of the coal pass out through an opening in the top to the hydraulic main and are thence conducted through a series of washers and scrubbers, as in the manufacture of gas, in order to remove the tar and ammonia. The purified gas is then allowed to pass into a holder from which it is drawn as needed for burning under the retorts. As the object of the coke manufacturer is to obtain the largest possible yield of coke from his coal, and as the quantity of gas produced is only a secondary consideration, he usually fires his retort at a comparatively low temperature, not much in excess of 1000° C. and sometimes considerably lower. This results in an increase in the yield of tar over that of modern gas manufacture and incidentally in an improvement in the quality of the tar for road purposes, as can be seen from the results of examination of two typical American coke oven tars

given below. It should be mentioned, however, that some coke ovens, particularly the Otto, are fired at higher temperatures and produce tars quite similar to gas house coal tars.

CRUDE COKE OVEN TARS.

| | (1) | (2) |
|-----------------------------------|------------------------|-----------------------------------|
| Character | Viscous, Smooth | Viscous, Smooth 1.167 |
| Ammoniacal water, per cent by vol | 15.9 31.5 | 1.0 1.0 6.0 32.8 59.2 |
| Pitch residue, per cent by weight | 100.0 52.4 6.70% | 100.0 64.7 8.56% |

Remarks.—In tar No. 1 the second light oil distillate showed only a trace of precipitated naphthalene when cold and the heavy oil distillate about one-half its volume precipitated naphthalene. In tar No. 2 the second light oils solidified when cold and the heavy oil distillate showed about one-half its volume precipitated naphthalene. The pitch residues from both showed a fairly lustrous fracture.

The two tars shown above were produced at comparatively low temperatures, as evidenced by their low free carbon content and rather low specific gravity. As in the case of crude gas house coal tars they contain ammoniacal water and light oils distilling below 110° C. While both of these tars show considerable quantities of naphthalene, the heavy oil fraction is large as in the case of the medium temperature crude gas house coal tar, so that a considerable amount of heavy fluid distillate is present. After deducting the free carbon, they both show higher percentages of pitch bitumens than do either of the gas house tars previously described. This is characteristic of low temperature tars and constitutes one of their chief advantages. Both of these materials could be refined to produce good binders for macadam road construction, as will be shown later. The low percentage of free carbon is characteristic of the Semet-Solvay coke oven tars, which usually carry from 3 to 10 per cent of this constituent. The Otto-Hoffmann ovens produce higher carbon tars as they are fired at a higher temperature.

Theory of Formation of Coal Tar Hydrocarbons. — The formation of coal tar hydrocarbons is an extremely complicated subject and a number of theories have been advanced by eminent chemists, none of which is entirely satisfactory. So many modifying factors have to be considered that it is doubtful if any one theory will ever be found to cover them all. In a book of this nature it is unnecessary to enter into a detailed discussion of these theories, but some of the most important should be briefly reviewed in order to give some idea of the differences in character of the various coal tars.

Besides the character of the coal itself, there are at least three important factors which affect the products of the destructive distillation of coal. They are time, temperature and pressure.

Little is known of the molecular composition of coals, although their ultimate composition has been determined in many instances and found to vary greatly in different samples. While coal is sometimes considered as a complex molecule, it is in all probability a complex mixture and the composition of the tar which it produces must necessarily vary with the character and relative proportions of the compounds which it contains and, therefore, with the ratio of hydrogen, carbon, oxygen, etc., to one another. It is definitely known that tar is not a simple mixture of the volatile constituents of the coal, but that it is the product of complex chemical reactions which take place during the process of carbonization. All chemical reactions are influenced by time, temperature and pressure and the formation of coal tar must, therefore, be influenced by these factors. As an actual example of the effect of temperature, reference may be made to a statement by Jayne:* "The influence of the temperature used in carbonizing is strikingly shown by the test of two tars, both from the same coal, and made in the same

^{* &}quot;The Coal Tar Industry in the United States." Paper presented to the Fourth International Congress of Applied Chemistry, June, 1903.

kind of ovens. One plant was producing gas as its main object. The tar from this plant had a gravity of 1.21 and tested 17.5 per cent of carbon; the light oil fraction was 2.2 per cent of a gravity 0.979, testing 23 per cent to 170 degrees; the total acids in the tar oils were 3.6 per cent and the dry pressed naphthalene 7.4 per cent. In the second tar, in which coke was the main object, evidently much lower heats were used, the tar having a gravity of 1.137 and testing 3.2 per cent of carbon; the light oil amounted to 11.9 per cent, and had a gravity of 0.970, testing 28 per cent to 170 degrees, or six times more crude naphtha than in first tar; the total tar acids were 12.48 per cent while the pressed naphthalene fell to 1.2 per cent. It is evident that in the first tar the light hydrocarbons and tar acids have been destroyed by the temperature employed with the formation of naphthalene."

The probable character of the reactions which take place in the retort have been very clearly stated by Fulweiler* as follows: "The carbonization of coal in any retort proceeds in three general stages:

"First. — There is a preliminary decomposition, which begins as soon as the coal has acquired a certain fairly definite temperature, and as this stage is quite strongly endothermic, approaching as it does a fusion, the temperature remains practically constant until completion.

"Second. — The products resulting from the first stage, which consist principally of the higher members of the chain, or aliphatic series, suffer very considerable molecular rearrangement. In general, since the C-H bond seems stronger than the C-C bond, compounds containing less than three atoms of carbon are formed. This stage may be looked upon as a continuance of the simplification in which every distillation results.

"These first two stages take place almost simultaneously within the charge itself and are both endothermic.

 $[\]ast$ " The Physical Theory of Coal Carbonization." Paper written for the Third Annual Meeting of the American Gas Institute,

"Third. — The gaseous vapors resulting from the second stage, when evolved from the protecting influence of the actual coal particles, are acted upon by the conducted and radiant heat of the more highly heated portions of the charge proper, of the sides of the containing retort and of the superheated surfaces above the coal (or free space).

"The reactions taking place at this stage are very complicated, depending, as they do, on the time of exposure and the temperature, and in some respects resemble a reversible reaction. The aliphatic hydrocarbons are on one hand loosening their carbon bonds and splitting off the initial members of their series, while the residues unite into more complex carbocyclic compounds. Thus benzol compounds under the heat influence in time are decomposed with the liberation of hydrogen, carbon and the formation of still higher ring compounds. On the other hand, the free hydrogen present reacts on the aliphatic compounds.

"It is this stage of the carbonization that is radically affected by the method of carbonization that is employed."

For a comprehensive consideration of the theories of the formation of the individual constituents of coal tar, reference should be made to the investigations of Berthelot, Jacobsen, Schulz, Kohler, Lewes, Mills, Bone and Coward and others who have made a study of this subject. While none of the theories which have been advanced is satisfactory in every respect, many of them are probably correct to a limited extent. The more complex hydrocarbons can be theoretically formed in a variety of ways and it would seem likely that they are thus formed under the varying conditions of temperature, pressure and time encountered during the process of carbonization. If during the first and second stages hydrocarbons containing less than three carbon atoms are formed, four possible compounds might be produced, CH4, C2H6, C2H4, and C₂H₂. Berthelot* considers that these compounds may combine and polymerize to form other compounds as follows:

^{* &}quot;Compt. Rend.," lxii, pp. 905-947.

While these reactions are purely speculative and open to serious criticism, they serve the purpose of showing the possible methods of formation of coal tar constituents. It is entirely probable that at high temperatures the hydrocarbons dissociate into radicals or residues such as CH≡, CH₂=, CH₃-, which under the varying conditions encountered in the distillation recombine in various ways to form other coal tar hydrocarbons, or else split up into the elements carbon and hydrogen. Such a theory has been advanced by Bone* and Coward and would at present seem to be the most generally acceptable. Upon such an assumption if nascent $C \equiv \text{and } H$ are included, the formation of the benzene homologues is conceivable either by direct union of these residues or according to the theory of Jacobsen, who assumes allyene (C3H4), the homologue of acetylene, to participate in the reactions. Thus the formation of C_3H_4 is made possible by the union of a $C \equiv$ with a CH≡ and a CH₃- residue, after which more complicated residue reactions might take place which could be expressed in condensed form according to Jacobsens' † reactions as follows:

2
$$C_2H_2 + C_3H_4 = C_7H_8$$
 toluene $C_2H_2 + 2 C_3H_4 = C_8H_{10}$ xylenes $3 C_3H_4 = C_9H_{12}$ mesitylene and pseudo-cumene.

^{*} London Journal, Aug. 4, 1908, p. 319. † Ber. Deutsch. Chem. Ges., 1877, p. 853.

Whatever the exact nature of these reactions may be, it is certain that at very high temperatures an ultimate decomposition of the hydrocarbons takes place with the formation of free carbon and free hydrogen. Any scrubbing action to which the highly heated vapors are subjected assists in this decomposition, and while the resulting hydrogen is found in the gas, a large proportion of the carbon is deposited in the tar. This decomposition undoubtedly occurs to the greatest extent when the vapors come in contact with the sides of the retort where the maximum temperatures prevail. The maximum temperatures may, therefore, be considered as responsible for the formation of free carbon in tars. This may be quite independent of the average temperature, as will be shown under the manufacture of water gas tar, where higher average temperatures are encountered but much lower maximum temperatures. It is because of lower temperatures that many coke oven tars contain less carbon than gas house coal tars.

Water Gas Tar. — The principle of making water gas is based upon the decomposition of steam by incandescent carbonaceous materials. Several reactions are involved according to temperature and pressure, with the ultimate formation of hydrogen and carbon monoxide. These reactions for the sake of convenience may be condensed to the following:

$$C + H_2O = CO + H_2$$

Ordinary water gas may, therefore, be considered as a simple mixture of these two constituents. As no hydrocarbons are formed in this process, there can be no formation of tar. Both hydrogen and carbon monoxide, however, burn with a non-luminous flame, which makes it necessary to enrich the water gas with hydrocarbons when it is desired to produce an illuminating gas. A petroleum product known as gas oil is commonly employed for this purpose and the resulting gas is said to be enriched or carburetted. In the carburetting process it becomes necessary to heat the oil in a peculiar way in order to produce permanent hydrocarbon gases. Other hydrocarbons

are formed at the same time, which pass over in a gaseous state, but later condense upon cooling to form the water gas tar. It will be seen that while such a tar is produced in the manufacture of carburetted water gas it is in reality an oil tar. Several methods of producing carburetted water gas have been suggested and used, but one known as the intermittent system has been most generally adopted. Following is given a brief description of this process, which is illustrated in Fig. 22.

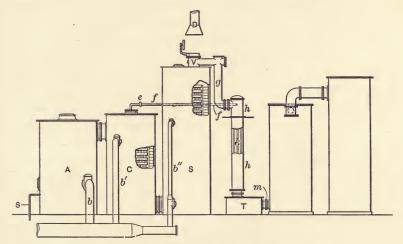


Fig. 22. Improved Low Carburetted Water-gas Plant.

Coke or anthracite coal is first heated to redness in a chamber A, called the generator. Air is then admitted to the generator through the blast pipe b, which passing through the incandescent fuel reacts with it to form producer gas. The hot producer gas passes out of the generator into the top of the chamber C, called the carburettor, where it meets a blast of air from pipe b', and is partially oxidized. The heat of combustion raises the temperature of the checkerwork of brick in C. The unconsumed gas and products of combustion next pass into the chamber S, known as the superheater. This chamber is also filled with a checkerwork of brick which becomes heated by contact with the gases, here entirely oxidized by air admitted through

the blast pipe b''. The products of combustion then escape through the stack valve V and pass up the stack D. This process is only preliminary to the actual manufacture of water gas and is continued just long enough to bring the fuel in the generator to a bright red heat and the brick checker work in the carburettor and superheater to proper temperature. When this is accomplished steam is admitted into the generator through the pipe s, all of the air blasts are shut off and the stack valve closed. Water gas is formed in the generator and passes into the carburettor, where it meets a spray of oil introduced through the pipe f. The oil is gradually gasified and carried by the water gas into the superheater, where it is broken up into permanent hydrocarbon gases by the high temperature, and also tarry products which condense during the process of gas purification. The enriched water gas passes from the superheater through the pipe g to a series of washers and scrubbers quite similar to those described under the manufacture of coal tar. Here the tarry products are deposited and afterwards run into storage tanks. The carburetting process is continued as long as the fuel in the generator is sufficiently high to produce good water gas. When it falls below this point the steam and oil are turned off, the stack valve opened, and the blast turned on in order to again heat up the system. When this is accomplished, the carburetting process is repeated, and so on.

Various oils are employed in the carburetting process, some being crude petroleum and some especially prepared petroleum products, known as gas oils. These gas oils are usually distillates falling between the illuminating oils and the lubricating oils. They vary greatly in character and therefore cause considerable variation in the tars which they produce upon being cracked. As in the formation of coal tar the characteristics of water gas tar are largely dependent upon the temperature at which it is produced. As a rule the maximum temperature is not sufficiently high to form any considerable amount of free carbon, but hydrocarbons are formed in much the same manner

as in the formation of coal tar and in many cases are identical with the coal tar hydrocarbons. The relative proportions of the various constituents are, however, quite different from the latter.

Crude water gas tar is a thin oily liquid having a specific gravity lying usually between I and I.I. It contains large quantities of water, from which it is often partially separated by mechanical devices not unlike a cream separator. This partially dehydrated tar is the crude water gas tar of commerce. It has a strong gassy odor, which, if it is used as a dust preventive, disappears shortly after application. Much of it is consumed as fuel by gas plants, being burnt under the boilers and retorts. Quite recently attempts have been made to refine it in much the same way that coal tars are refined. Valuable products have thus been obtained, both as distillates and residues. The properties of an average sample of crude water gas tar, from the standpoint of road treatment, are shown below.

CRUDE WATER GAS TAR.

| Character | Thin, oily |
|---|---------------|
| Water | 2.4 |
| First light oils to 110° C., per cent by vol | 3.5 |
| Second light oils 110°-170° C., per cent by vol | 18.1 |
| Heavy oils, 170°-270° C., per cent by vol | |
| Pitch residue (by difference) per cent by vol | 24.0 |
| | |
| | 100.0 |
| Pitch residue (per cent by weight) | 26.2 1.60% |
| Tice catbon | 1.00% |

Remarks. — The second light oils showed only a very small amount of precipitate naphthalene when cold, and the heavy oils none at all. The pitch residue showed a very lustrous fracture.

As compared with crude coal tars it will be seen from the above results that crude water gas tar is a very much lighter product, the specific gravity being below the lowest limit of coal tar. The water which it contains is practically free from ammonia, and this is characteristic of the material. It will be noticed that all of the distillates are comparatively free from

naphthalene, and this in connection with the low free carbon contents makes it a very satisfactory material to refine, in so far as the production of a road binder is concerned. The high percentage of heavy oils and low percentage of pitch residue make it an exceedingly poor binder in its natural condition. It has, however, valuable properties as a dust preventive and can be satisfactorily applied by means of an ordinary watering cart. It compares very favorably with some of the lighter petroleum products and emulsions when used for this purpose. Its odor is rather disagreeable at first, but disappears shortly after application has been made to a road surface. When mixed in suitable proportions with crude coal tar it forms a good temporary binder, which may be applied cold. Its greatest value for road purposes, however, is its ability to produce a very excellent soft tar pitch when properly refined.

In many gas plants it is the custom to manufacture both coal gas and carburetted water gas. When this is done the coal gas is produced at a high temperature in order to obtain the maximum yield, and the carburetted water gas is used to raise its illuminating value. In such plants the coal tar is unsuited for road work. Sometimes both the water gas tar and coal tar are run together into the same well, thus producing a mixture of the two. This mixture will be of an inferior quality for road treatment for reasons which have been previously discussed. It may, however, sometimes be distilled to produce a fairly good road binder. This is largely dependent upon the amount of water gas tar present, which serves to cut down the percentage of free carbon in the refined product.

Oil Gas Tar. — Tars formed in the manufacture of straight oil gas require but passing mention, as they are not produced in very large quantities and have not to the author's knowledge been used to any extent in the treatment of roads. There are a number of processes for producing oil gas, the most common being the Pintsch system and the Peebles process. They are all dependent upon the cracking of oil vapors in especially constructed retorts, with the formation of permanent gases and

tarry condensations of varied character. In some of these processes the tar itself is again cracked, so that in the end little but hydrocarbon gases and free carbon are produced.

The Effect of Free Carbon in Tars. — The effect of free carbon in tars from the standpoint of road treatment has been studied by the author and the results of his investigations presented in a recent paper,* which is quoted below at some length.

If a drop of tar is examined under the microscope it will be seen to consist of a more or less homogeneous liquid, which by transmittant light gives a reddish brown color, and in which float small black amorphous particles. It will also be noticed that the number of these particles varies enormously with different samples of tar. Under high magnification some of these particles or clumps of particles resemble irregular shaped lumps of coal, while others are so small as to be almost submicroscopic. If a small quantity of tar is diluted with a proper solvent, such as benzol or carbon bisulphide, the solution passed through a filter and the residue which is retained upon the filter thoroughly washed with the solvent, a black amorphous powder will be obtained, which, when examined under the microscope, can be identified as the floating particles which were found to exist in the original tar. This material is commonly known as free carbon.

The presence of free carbon in any considerable quantity may affect the physical properties of tars in two ways: (1) either mechanically by its actual presence or (2) by the presence of other substances which were formed with it at high temperatures. To test its mechanical effect a gas house tar was selected which was found to contain 29.2 per cent free carbon. A quantity of this tar after dehydration was diluted with coal tar benzol and quickly filtered through a folded filter paper in order to remove most of the free carbon. The filtrate was then evaporated on a steam bath beside a fresh sample of

^{* &}quot;The Effect of Free Carbon in Tars from the Standpoint of Road Treatment." Proceedings of the American Society for Testing Materials, Vol. IX, 1909, p. 549.

the dehydrated tar until no odor of benzol could be detected in either sample, and the evaporation continued until both samples showed the same rate of flow and approximately the same consistency as determined by the float test.

Determinations made upon the filtered and unfiltered tars, prepared in the manner described, showed them to contain 4.4 per cent and 31.0 per cent free carbon respectively. By mixing proper proportions of these tars two other samples were obtained, one of which held 10 per cent and the other 20 per cent free carbon. The samples were then given numbers from I to 4 as the free carbon contents increased. The relative cohesive or binding strength of these samples was next determined by means of a machine especially designed for this pur-The results as given in Table I show the maximum resistance in pounds, which was offered to a breaking load applied in tension to a layer of the tar held between two metal surfaces, the reading being obtained by means of a spring balance to which one of the metal contacts was attached. The thickness of the layer of tar was identical in every test, as well as all other conditions, such as temperature, etc., so that the results obtained are strictly comparable.

TABLE I.

| Sample No | I | 2 | 3 | 4 |
|-------------|--------|---------|-------|-------|
| Free carbon | 4.4% | 10.0% | 20.0% | 31.0% |
| | 18 lb. | 7.5 lb. | 4 lb. | 3 lb. |
| | 19 lb. | 8 lb. | 4 lb. | 3 lb. |

From this table it will be seen that the cohesive or binding strength is almost inversely proportional to the amount of free carbon present. It should be remembered, however, that these tars are of approximately the same consistency and obtained from the same source, and that this relation would not necessarily or even probably hold good for different tars of different consistencies.

While the binding strength of a tar is one of its most important properties from the standpoint of road treatment, there are others fully as important. Its waterproofing quality when employed in a mineral aggregate should be considered, and for this purpose a number of sand-tar briquettes were made up with equal quantities of tar and their absorption in water determined.

The sand used in this and all of the other sand-tar experiments was a common river sand which had been thoroughly dried and passed through a 10 mesh sieve. It was found to contain 37 per cent voids when consolidated, and when mechanically separated showed the following percentage of various sized grains. Its specific gravity was 2.68.

| | | | | | _ | | _ | - | Sa — | no | 1. | _ | _ | _ | _ | | _ | _ | _ | | _ | _ | _ | _ | _ | _ | Per | cent |
|--------|-------|------|-------|----|---|------|---|---|---------|----|----|-------|---|----|---|------|---|-------|---|--|----|---|---|---|---|-------|-----|------|
| Passin | g 200 | mesh | sieve | e | | | | | | | | | | | | | | | | | | | | | | | | 6 |
| " | 100 | " | " | | | | | | | | | | | | | | | | | | | | | | | | | 2 |
| " | 80 | " | " | | | | | | | | | | | | | | | | | | | | | | | | | 2 |
| " | 50 | 66 | " | ٠. | | | | | | | | | | | | | | | | | | | | | | | | 18 |
| " | 40 | 66 | 44 | | | | | | | | | | | | | | | | | | | | | | | | | 8 |
| " | 30 | " | " | | | | | | | | | | | | | | | | | | | | | | | | | 38 |
| " | 20 | 66 | " | | • | | | | | | | | | ٠. | | | | | | | ٠. | | | | • | | | 26 |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | ı | 00 |

The sand-tar mixtures were carefully prepared in metal cups heated by means of a low flame in such a manner that at all times the handle of the cup could be held without burning the flesh. But very little loss by volatilization, therefore, occurred.

In the following experiments 6 parts by weight of tar were stirred with 100 parts by weight of sand, until the mixture was to all appearances absolutely uniform. While still warm the mixtures were pressed by hand into ordinary cement molds and allowed to cool. They were then removed from the mold, weighed and placed under water for 24 hours, after which they were drained free from surplus water, wiped with a soft towel and again weighed. The gain in weight was calculated upon a percentage basis as water absorbed, and the results so obtained are given in Table II.

TABLE II.

| Sample No | 1 | 2 | 3 | 4 |
|--------------------------------|---|-------------------------|-------------------------|--------------------------|
| Per cent free carbon in binder | | 10.0 110.64 4.15% | 20.0 109.35 6.19% | 31.0 109.12 10.99% |

It will of course be noticed that the percentage of water absorbed increases with the percentage of free carbon present in the binder. The same modifying factors mentioned under the binding strength tests, however, should be considered in connection with the above results.

While all of the tar samples in the preceding tests were of about the same consistency, it was realized that the actual bitumen contained could not be of the same consistency in the different samples, for the reason that if a quantity of any inert power is added to a tar the consistency of the mixture will be greater than that of the original tar. In order to obtain some idea as to the mechanical effect of free carbon upon tar bitumens of a given consistency, a dehydrated coke oven tar, called sample 5, containing 7.0 per cent free carbon, was selected and to a portion of this tar lampblack was added in quantity sufficient to raise the free carbon contents to 25 per cent. This mixture was called sample 6. The use of lampblack as a substitute for free carbon is certainly subject to criticism, but it was selected by the writer as more nearly resembling free carbon than anything else that could readily be obtained. The addition of this substance increased the consistency of the tar considerably, and determinations of the relative binding strength of the two samples made in the manner previously described showed a considerable gain in strength for the tar to which it had been added. The results so obtained are given in Table III. These tests would seem to show that the presence of free carbon in tar bitumens of a given consistency increases the cohesive or binding strength of the material.

TABLE III.

| Sample No | 5 | 6 |
|--|-----------------------------|------------------------------|
| Free carbon. Binding strength at 25° C., Test 1. Binding strength at 25° C., Test 2. | 7.0% 13.5 lb. 13 lbs. | 25.0% 20+ lb. 20+ lbs. |

Note. - Twenty pounds was the limit of the machine.

Sand briquettes were next made with these samples, as in the other tests, using 6 parts by weight of tar to 100 parts by weight of sand. While the briquette made with No. 5 could be handled without breaking, that made with No. 6 would not hold together, showing that, notwithstanding the fact that the binding strength of the tar had been increased by the addition of carbon, its binding capacity had been diminished. In order to compare the relative waterproofing qualities of these two materials, it was found necessary to make a briquette with No. 6 which should have a bitumen equivalent of No. 5, and this was accomplished by using 7.44 parts of No. 6 in place of 6 parts. From the results of these absorption tests made in exactly the same manner as described in the other experiments it will be seen that here again the percentage of water absorbed increases with the percentage of free carbon contained in the binder. These results are given in Table IV.

TABLE IV.

| Sample No | 5 | 6 | |
|-------------|-------|----------|-------|
| Free carbon | 7.0% | 25.0% | 25.0% |
| | 6.00% | 6.00% | 7.44% |
| | 1.94% | Crumbled | 3.77% |

When applying tar to an old road surface, to insure lasting results it is most important that the tar should penetrate the surface of the road to a considerable extent. To determine the effect which free carbon would have upon this property three coal tars containing different amounts of free carbon were selected. These tars were numbered 7, 8, and 9, in the order of their free carbon contents, and were painted upon unglazed porcelain tiles, the thickness of each coat being made as nearly the same as possible. After the painted surfaces had dried off, the tiles were broken and the average penetration measured. The results so obtained are given in Table V, and indicate that free carbon seriously affects the penetrating value of tars.

TABLE V.

| Sample No. | 7 | 8 | 9 |
|---|-----|-------------------------|-------------------------|
| Free carbon. One coat of tar penetration. Three coats of tar penetration. | 4 " | 29.2% 2" 64 5" | 30.9% 2" 64 5" |

The surface coat of bitumen was next scraped from the tiles with a knife. No. 7 was very sticky and difficult to remove, Nos. 8 and 9 could, however, be readily peeled off, and the skin of bitumen thus obtained was in each case much less sticky than No. 7 and quite short.

With the exception of the tile tests all of the experiments so far described have had to do with the mechanical effect of free carbon on practically the same kind of bitumen. The fact that differences in character of the bitumens found in low and high carbon tars may affect the physical properties of the tars has already been mentioned, and in order to study the effect of both together, representative samples of low, medium and high carbon tars were taken for the following experiments. As the consistency of the tars employed in the preceding experiments was not great enough to produce sand-tar briquettes which could be successfully tested for strength, it was thought advisable to reduce these tars to the consistency of medium soft pitches, such as might be employed in road construction. While the penetration test is usually employed to determine the consistency of such materials, the melting point as determined by

the well-known cube test is generally used in grading pitches, and for a number of reasons it was decided to make use of this test as a basis of comparison. In the first place, if all of the samples were found to have the same penetration at a given temperature it would not necessarily follow that they would have the same relative penetration at another temperature. Moreover it was feared that the presence of free carbon would seriously affect the movement of the needle, so that the actual consistency of the bitumen present would not be indicated. By experiment this was found to be true at ordinary temperatures, although at low temperatures the effect of the carbon appeared to be lessened. On the other hand, the melting point was believed to more nearly represent the actual consistency of the bitumen present. For the sake of comparison, however, results of both the penetration and float tests are given in Table VI.

TABLE VI.

| Sample No. | 10 | 11 | 12 |
|---|------------------------------|---------------------------------|---------------------------------|
| Kind of tarFree carbonMelting point | Water gas 1.60% 50° C. | Coke oven 12.00% 50° C. | Gas H. 35.70% 50° C. |
| PENETRATION TESTS. No. 2 needle, 5 sec., 100 gms., 25° C. No. 2 needle, next 5 sec., 100 gms., 25° C. No. 2 needle, next 5 sec., 100 gms., 25° C. No. 2 needle, 1 min., 200 gms., 5° C. Float test at 60° C. | 16 . 12 6 | 50 22 17 6 185 sec. | 56 24 20 6 334 sec. |

The tars selected were a Philadelphia water gas tar called sample 10, a Birmingham coke oven tar called sample 11, and a Providence gas house tar called sample 12. Fairly large portions of these materials were evaporated in a hot air oven until their melting points were 50° C., the temperature of the oven at no time being allowed to exceed 250° C. Sand tar mixtures with varying proportions of binder, as shown in tables VII and VIII, were then made up, and these mixtures molded into briquettes in the following manner.

Twenty grams of the mixture was weighed out and placed in a cylindrical metal mold carrying a close fitting plunger. Pressure was then applied by means of a small Olsen Testing Machine run at a constant speed. All of the mixtures were subjected to a pressure of 1425 lbs. and the briquettes thus formed measured 25 mm. in diameter and approximately 25 mm. in height. There was no particular reason for making the briquettes in just this manner, except that the method conformed to the general method employed by the Office of Public Roads in making rock dust briquettes for the cementation test.

As soon as they were made three briquettes of each mixture were placed in a refrigerator for 30 minutes, after which they were immersed in ice water at 5° C. for 30 minutes and tested under water at this temperature in the Olsen Testing Machine, which was run at a definite speed. Tests were made in compression, and the maximum resistance offered by the briquettes noted. Check tests of the same mixtures varied somewhat, as shown in the following tables, but it is believed that a comparison of the average results will prove of considerable value in determining the effect of free carbon upon the binding values of the tars. Slight variations in the method of making the tests were found to cause considerable variations in results, so that it was necessary to take every precaution to duplicate the exact conditions under which each of these tests were made.

The following tables are self-explanatory, so that it seems unnecessary to describe them further than to say that two series, one with 6 per cent binder and the other with 10 per cent binder, were made in such a manner that comparisons upon both a percentage binder and maximum and minimum percentage bitumen bases could be drawn. In these briquette tests the percentage of all constituents is based upon the weight of sand taken as 100.

In considering the compression tests in Table VII it will be seen that for equal quantities of binder the low carbon tar has a greater binding strength than either of the others, and that the medium carbon tar gives higher results than the high carbon

TABLE VII.

| Comparative Basis | | Per cent Tar. | ar. | Мах. | Max. Per cent Bitumen. | itumen. | Min. P | Min. Per cent Bitumen. | umen. |
|-----------------------|--|---|---|--|---|--|---|--|--|
| Sample No | IO | II | 12 | OI. | II | 1.2 | Io | 11 | 12 |
| Free carbon, per cent | 1.60 6.00 5.90 7.90 **339 *3373 *377 | 12.00 6.00 5.28 7.72 7.74 7.74 7.75 8.355 8.355 | 35.70 6.00 3.86 3.86 1141 1142 1138 7.05 | 1. 60 6.00 5.90 7.10 8.330 8.373 8.377 8.44 | 12.00 6.70 5.90 8.80 8.476 *4465 4465 5.28 | 35.70 9.17 5.90 3.27 4619 4617 4592 609 5.58 | 1.60 3.93 3.86 3.86 4.184 4.156 4.156 6.66 | 12.00 4.39 3.86 53 1146 1196 1200 181 6.44 | 35.70 6.00 3.86 3.14 2.14 2.14 2.142 1.123 1.168 |

* Briquette was deformed but not broken by maximum load. † Briquette was broken by maximum load. ‡ Briquette crumbled under maximum load.

TABLE VIII.

| len. | 1.2 | 35.70 | 6.43 | .00 | 6.39 | 645 | 644 | 6.43 | 1.02 | 1.25 | 1.45 | 10.15 |
|---------------------------|-----------|----------------|---|--|--|---|-------------|---|------|--|---------------------------------------|----------------------|
| 3itum | | 1 33 | 88 | | | | 902 | | | 1 | | <u>.</u> |
| ent I | 111 | 7.31 | 43.8 | 2.69 | 661 | 65 | 2.67 | i | : | : | : | : |
| Per c | | 12. | . 6.43 | : : | 492 | 483 | 489 | 4.70 | 1.23 | 1.27 | I.40 | 8.60 |
| Minimum Per cent Bitumen. | | 0.80 | 3.10 | 3.57 | 583 | 615 | 608 | 4.70 | 1.23 | 1.27 | | 8.60 |
| Mir | 10 | 1.60 | 6.43 | | 446 | 422 | 428 | 4.03 | .95 | 1.35 | 1.66 | 7.99 |
| umen. | 12 | 35.70 15.30 | 9.84 | 5.46 | 772 | . 012 | 750 | 5.22 | 1.32 | 1.09 | 1.07 | 8.70 |
| nt Bit | | 12.00 | 9.84 4 I.34 | 4.12 | 995 | 804 | 896 | : | : | : | : | : |
| Per ce | 11 | 12. | .3 | | 842 786 | 064 | 806 | 4.34 | 1.15 | 1.03 | 1.04 | 95.2 |
| Maximum Per cent Bitumen. | 10 | 1.60 | ,0 | 5.30 | 888 | 800 | 844 | | 1.15 | 1.03 | : | 7.56 |
| Ma | I | . I . | 9.84 | : : | 765 | 740 | 755 | 2.52 | 1.08 | 98. | 1.04 | 5.50 |
| ar. | 1.2 | 35.70 | 6.43 | :: | 639 648 | 645 | 644 | 6.43 | 1.02 | 1.25 | 1.45 | 5.50 7.30 10.15 5.50 |
| Per cent Tar. | 11 | | 9.84 8.80 | | 7.06 | 648 | 682 3.93 | 3.69 | 1.27 | 1.15 | 61.1 | 7.30 |
| Per | o I | 1.60 12.00 | 9.84 | : : | 765 | 740 | 755 | 2.52 | 1.08 | 98. | 1.04 | 5.50 |
| Comparative Basis | Sample No | Free carbon | Cent. Amount of carbon in briquette, per cent Amount limestone dust in briquette, per | Amount total filler in briquette, per cent | Resistance to compression (1), pounds Resistance to compression (2), pounds. | Resistance to compression (3), pounds Resistance to compression (average). | pounds | volatilization, 1st 5 nours, 100° C., per cent. | ٠. | cent. Volatilization, 4th 5 hours, 100° C. per | Volatilization, 20 hours, 100°C., per | cent |

Note.—In the compression tests all of the briquettes were deformed, but not broken by maximum load. Loss by volatilization is given upon the basis of bitumen present in the briquette.

tar. For equal quantities of bitumen on the basis of the minimum amount present, as shown by No. 12, results are nearly the same for all of the tars. Upon a maximum bitumen basis as shown by No. 10, the results are, however, reversed. The explanation for this lies in the fact that when considerable quantities of free carbon are present the carbon acts as a filler and adds to the mechanical strength of the mineral aggregate. This is shown in Table VIII under the heading Minimum Per Cent Bitumen, in which the percentage of bitumen is almost the same as in the last tests mentioned in Table VII. It will, however, be noticed that where an amount of limestone dust is added in sufficient quantity to produce an equivalent weight of filler that the strength developed by the same per cent of bitumen is again almost the same for the different tars. is an important consideration from the standpoint of road construction.

In Table VIII, where an equivalent amount of binder is employed, it will be seen that the same general relations hold good as shown under similar conditions in Table VII. The differences are, however, not so marked because of the more prominent part played by free carbon as a filler. It should be remembered, however, that in ordinary bituminous macadam construction over 6 per cent bitumen is seldom employed in the mineral aggregate, and that as this aggregate is much coarser than the sand used in the tests, the action of the relatively small amount of carbon as a filler is hardly worth considering. The results given in Table VIII under the heading Maximum Per Cent Bitumen, tend to show much the same thing as the Minimum Per Cent Bitumen Tests, although here the high carbon tar shows up to even less advantage. Considered as a whole these tests show the mechanical effect of free carbon, but would not seem to indicate that the bitumen present in low and high carbon tars varies greatly in binding value.

Absorption tests made upon these briquettes show in both Tables VII and VIII that where equivalent quantities of binder are employed those briquettes which are made with the

high carbon tar are somewhat less waterproof than the lower carbon tars. In Table VII the same general relations seem to hold good for the maximum and minimum bitumen tests, but in Table VIII in the bitumen equivalent tests the excess of bitumen coated carbon seems to have lowered the absorptive capacity of the briquettes. A still further lowering is, however, observed where limestone dust has been added in the briquettes made with low carbon tars, and the superiority as a filler of limestone over carbon again indicated. In considering these tests as a whole it might be remarked that a slight superiority in waterproofing power, of the bitumens contained in No. 11 over the other tars is indicated, although this difference is by no means great.

One other important property of tars from the standpoint of road treatment which has not yet been considered is the relative amount of volatilization which may be expected to take place on a tar treated road. Some of the constituents of all tars will volatilize at ordinary temperatures, thus making the residue more and more brittle and lessening its life. It is believed by some that the presence of free carbon retards this volatilization, and the reason for this belief lies in the fact that in both evaporation and distillation tests a film of carbon forms upon the surface of the hot tar and retards to a considerable extent the volatilization of the lighter constituents. In evaporating the three tars which were employed in all of the later tests, this effect was made very evident by the time required to bring No. 12 to the proper consistency as compared with that necessary to bring the other samples to the same consistency. When tar is employed in road work, however, conditions are somewhat different, for here the tar does not exist in thick layers, but is distributed over the surface of the particles composing the mineral aggregate in comparatively thin films. In order to determine whether or not free carbon retards volatilization under these conditions, it was thought well to subject some of the sand-tar briquettes to a volatilization test. Briquettes composed of different mixtures were therefore carefully weighed upon watch glasses and

placed in a hot air oven maintained at a uniform temperature of 100° C. for four consecutive periods of five hours each. loss in weight for each period was determined and the percentage loss upon the basis of bitumen present, calculated. results so obtained are given in Table VIII. The first fact to be noted is that the greatest loss in every case occurred during the first period, and that the greatest differences between individual tests are here made apparent. During the next three periods the loss by volatilization seems to be practically constant and quite uniform for the different briquettes. In the first period it will be noticed that the higher the percentage of free carbon the greater the loss by volatilization, and if these results alone were considered one might naturally come to the conclusion that the presence of free carbon increased the volatility of the tar. In view of the general uniformity of the next three tests this opinion would have to be modified, and the only reasonable conclusion would seem to be that under the given conditions free carbon is mechanically inert so far as volatilization is concerned. It would seem, however, that in tars of the same melting point the percentage of highly volatile constituents increases as the percentage of free carbon increases, and that a greater loss by volatilization would occur in high carbon tars than in low carbon tars under conditions encountered in tar treated roads. That the thickness of the tar film has considerable effect upon the volatility of the tar is indicated by the fact that in nearly every case less loss by volatilization occurred in the maximum bitumen tests than in the corresponding minimum bitumen tests. In this connection it might be said that one of the advantages of employing a flush coat of tar in bituminous road construction is made apparent, as a coat so applied retards the volatilization of the thinner underlying films of tar, and therefore prolongs the life of the road.

Before summarizing the results of the experiments presented in this paper it may be well to mention one other property of tars and its possible relation to the free carbon contents, *i.e.*, the relative susceptibility to temperature changes shown by bitumens contained in different tars. Owing to the fact that free carbon if present in any quantity seriously interferes with a correct determination of the consistency of the accompanying bitumen, it would seem necessary to completely remove the carbon before attempting to determine the susceptibility of the bitumen to temperature changes. As such bodies as naphthalene and anthracene, which crystallize at comparatively high temperatures, usually occur in greater quantities in high carbon than in low carbon tars, it would seem reasonable to suppose that the bitumen obtained from the former would be more susceptible to temperature changes. This is an important point to be determined and one which the writer proposes to follow up. As it is only indirectly related to the subject of this paper it will not be further discussed at this time.

Upon reviewing all of the results presented it is believed that the following facts have been demonstrated with respect to the effect of free carbon in tars:

- (1) That in tars of the same consistency those of low carbon contents have a greater inherent binding strength than those of high carbon contents.
- (2) That in tars whose bitumen contents are of the same consistency those of high carbon contents have a greater inherent binding strength than those of low carbon contents, but that the binding capacity of the former is lower.
- (3) That in sand-tar mixtures containing a relatively large amount of high carbon tar, the carbon may act as a filler and add to the mechanical strength of the mineral aggregate, but that better results in this respect can be obtained by the use of a smaller quantity of low carbon tar of the same melting point, together with a mineral filler.
- (4) That the waterproofing value of high carbon tars is in general less than that of low carbon tars.
- (5) That free carbon retards the absorption of tars by porous surfaces.

(6) That when tar is exposed in comparatively thin films free carbon has little or no effect in retarding volatilization.

Applying these facts to the use of tar in road treatment the following conclusions are logically deduced:

- (1) In the treatment of old road surfaces a low carbon tar is to be greatly preferred to a high carbon tar.
- (2) In ordinary bituminous road construction, both from the standpoint of efficiency and economy, a low carbon tar is to be preferred to a high carbon tar whose bitumen content is of the same consistency.

In conclusion it might be said that to the writer's knowledge no reliable comparative data as to the actual service results obtained by the use of high and low carbon tars in road work is at present available. A road engineer in one locality may have obtained more satisfactory results from the use under certain conditions of a high carbon tar of a certain consistency than another engineer in a different locality using a low carbon tar of different consistency under different conditions, and vice versa. Many other factors besides the free carbon contents have to be considered in forming a correct opinion of the relative value of two tars. The writer also realizes that laboratory results do not always conform to actual service results, but they are nevertheless often of considerable value to those who are studying a subject from a practical standpoint. It might be added that results so far obtained seem to substantiate the general conclusions presented in this paper.

Tar Refining. — With the development of the coal tar industries the refining of crude tars has become necessary, and a great deal of tar now produced is subjected to fractional distillation for the separation of certain constituents which are used in the arts. The method of distillation varies somewhat as the market value of the distillates fluctuates. Germany is greatly in advance of this country at the present time in refining tar, and a brief consideration of the general method employed in that country should be of value in obtaining some idea of

its various constituents. For a full consideration of the process of tar refining reference should be made to a treatise on the subject by Lunge.*

The ordinary refining still consists of a vertical wrought iron cylinder with a dome-shaped top and concave bottom, as shown in Fig. 23. The top is provided with an inlet A for the

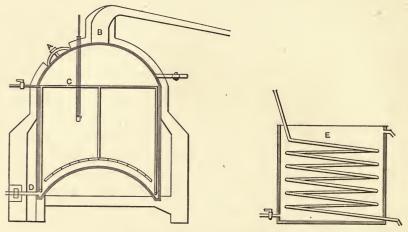


Fig. 23. German Type of Tar Still and Condenser.

tar, and a large curved outlet pipe B for the vapors, the concave bottom facilitating the distribution of heat into the interior of the charge of tar. The still is fire heated at first, but toward the end of the process superheated steam is forced through the coil C to aid in the distillation of the heavier products. A draw-off D allows the residual pitch to be removed while hot. These stills have a capacity of from ten to twenty tons. The outlet pipe leads to the condenser E, which is an iron or lead worm placed in a tank of water. The operation of distillation or fractionation consists in heating the charge of tar carefully until drops of liquid come from the still. The fire then has to be moderated until all volatile material up to 105° C. is removed in order to prevent boiling over. As the more volatile products are removed the temperature rises, and

^{* &}quot;Coal Tar and Ammonia." Gurney and Jackson.

the point where distillation is stopped depends upon the products which it is desired to obtain. Usually five fractions are produced: (1) First runnings to 105° C. containing ammonical liquor and first light oils; (2) second light oils from 105° to 210° C.; (3) carbolic oils from 210° C. to 240° C.; (4) heavy, dead, or creosote oils 240° C. to 270° C., and (5) anthracene or green oil above 270° C. All of these fractions are more or less contaminated with portions of the other fractions which are carried over or held back mechanically, and have to be themselves subjected to further distillation in order to obtain purer substances. The light oils are distilled for benzol and naphtha; the carbolic oils are treated to obtain carbolic acid and naphthalene, which is largely found in this distillate; the creosote oils also contain naphthalene, for which they are sometimes treated; and from the green oil anthracene is separated. The residue left in the still is known as coal tar pitch and is a thick, viscous material while hot. It represents the true binding base of the tar, and, if the tar is one produced at a comparatively low temperature, is composed mainly of bitumens. After cooling somewhat it is run out of the still into a smothering chamber, and after further cooling is drawn off, and graded as soft, medium, or hard, according to its condition when cold. The dead oils, which are of the least value of any of the fractions, are often run back into the still before the pitch is drawn off. In this case the pitch is liquid when cold. Besides the three grades mentioned there are numerous intermediate varieties which have their own particular use in the trades. These pitches are graded according to their so-called melting point. Liquid pitch is often used as a paint for wood and metal work and for making tarred or roofing paper, while the harder pitches are employed as cements or mastics and find their place in the road and paving industries in competition with the natural bitumens. the coal tar has been previously manufactured at an exceedingly high temperature, all of the free carbon or lampblack which was originally deposited in the tar will be found in the pitch. Its waterproofing and adhesive properties will therefore

be lessened and any preparation containing this pitch as a base will be correspondingly poor for use as a road binder.

Naphthalene is one of the most important constituents of coal tar and is consequently recovered from the various distillates. When pure it exists in shining white plate-like crystals which volatilize slowly at ordinary temperatures. It has a pungent, camphor-like odor and is employed in the manufacture of moth-balls. Its most important use, however, is in the preparation of coal tar dyes. Its removal from the tar is undoubtedly of advantage in the preparation of a road binder as it has none of those qualities requisite for a good material of this nature. The same may be said of anthracene, which is probably the most valuable constituent of coal tar and is, therefore, removed from the fractions in which it is found. It is employed entirely in the preparation of alizarine, a valuable coloring material.

In the United States but comparatively few gas companies make any attempt to distill their crude tar, but sell it to those who make a business of tar distilling. The tar is either transported by rail in large tank cars or by water in tank barges. The distiller stores his tars in large iron tanks until ready for use. The upright stills previously described are seldom employed, but in their place large horizontal cylindrical stills often holding as much as 25,000 gallons are employed. They are quite similar to the stills used in the oil industry. It is customary to divide the fractions into only two portions, the light oils, having a specific gravity of less than 1.00, and the heavy oils, having a gravity greater than 1.00. Distillation is often carried only to the point where a residue of the desired consistency is obtained. These residues may be either fluid, semisolid or solid at ordinary temperatures. If semisolid or solid they are termed pitch, and graded according to their melting points. Sometimes distillation is carried to the formation of what would be a hard pitch if allowed to cool, but while still hot sufficient heavy or dead oils are run back into the still to produce a pitch of any desired consistency. Such materials are called

cut-back products and for road purposes are usually superior to the straight residues, for before running back the dead oils it is customary to remove most of the naphthalene which they contain. Sometimes water gas tars and coal tars are blended before being distilled, usually for the purpose of controlling the free carbon contents of the residue. The blowing of tar pitches has also been resorted to in the preparation of road products, particularly in the distillation of water gas tar.

Dehydrated Tars. — Sometimes only dehydrated tar is prepared for use as a dust preventive and semipermanent binder, the idea being to remove all water, ammonium compounds and some of the light oils. A preparation of this kind is to be preferred to the crude tar, as the absence of water makes it easier to handle when applied hot and probably allows of a better absorption of the tar by the road surface. If much water is present in the tar, it is absorbed by the road material in preference to the tar and thus becomes to a certain extent tar proof. As a result the tar is very likely to peel after application. Water in the tar itself will also hasten disintegration of the heavy binding materials during the course of time. The ammoniacal liquor may saponify some of the oily products which are then capable of mixing with water and, therefore, apt to be washed out. The results of examination of a dehydrated road tar suitable for cold applications are given below:

DEHYDRATED ROAD TAR.

| CharacterTh | in, oily |
|---|----------|
| Specific gravity | 1.086 |
| Distillation: | |
| Water, per cent by vo | 0.0 |
| First light oils, to 110° C | 7.5 |
| Second light oils 110°-170° C., per cent by vol | 10.5 |
| Heavy oils, 170°-270° C., per cent by vol | 42.0 |
| Pitch residue (by difference), per cent by vol | 40.0 |
| | 100.0 |
| Pitch residue (per cent by weight) | 42.0 |
| Free carbon | 0.66 |

Remarks. — None of the distillates contained more than a trace of precipitated naphthalene when cold. The pitch showed a lustrous fracture.

From the low specific gravity and free carbon contents as well as the absence of appreciable quantities of naphthalene it is evident that this is a dehydrated water gas tar. Its superiority for road purposes over the crude tar described on page 249 is not only due to its lack of water, but also to the presence of a larger amount of pitch. Such a material will prove very suitable as a dust preventive and temporary binder when employed in the surface treatment of macadam roads.

Residual Tars. — Residual tars, as has been stated, are those from which the lighter products have been removed by distillation. They may be of any consistency from very fluid to solid. Only the fluid and semisolid tar pitches are employed in road treatment, as the solid varieties are too brittle to prove satisfactory. The properties of three typical residual road tars, the first two of which are trade products, are given in the following table:

RESIDUAL ROAD TARS.

| | I | 2 | 3 |
|---|---------------------|------------------------------|------------------------------|
| Character | Viscous, Smooth. | Semisolid, Fairly Smooth. | Semisolid, Fairly Smooth. |
| Specific gravity, 25°/25° C | Fluid | 1.248 26° | 1.239 |
| Distillation: Water First light oils to 110° C., per cent | 0.0 | 0.0 | 0.0 |
| by vol | Trace | .0 | 0.0 |
| cent by vol | | 1.2 | •4 |
| by vol | 47.6 | 20.2 | 33.1 |
| by vol | 39.6 | 78.6 | 66.5 |
| | 100.0 | 100.0 | 100.0 |
| Pitch residue (per cent by weight). | | 82.3 | 71.0 |
| Free carbon | 11.2 | 23.95 | 20.19 |

Remarks. — In sample 1 the light oils were free from precipitated naphthalene when cold, while the dead oils showed one-third their volume of this constituent. The fracture of the pitch residue was fairly lustrous. In No. 2 the light oils showed about one-half their volume precipitated naphthalene and the heavy oils about two-fifths. In No. 3 the heavy oils showed two-thirds their volume precipitated naphthalene. The pitch residue for both 2 and 3 showed a rather dull fracture.

Upon comparing these residual tars with the crude tars on pages 237 and 241, it will be seen that the water and first light oils of the latter are absent and that with the exception of No. 1 the percentage of second light oils is very much lower. The specific gravity of a residual tar is not necessarily greater than other crude tars, although it is higher than the original crude tar from which it was produced. The free carbon content of the residue is also greater than of the original crude material.

As compared with the other two tars, No. 1 is a much more fluid residue, as shown by the relative proportion of oils and pitch. The presence of a greater amount of second light oils shows either that distillation has not been carried so far as in the other two tars or that it is a cut-back product. The latter fact might be indicated by the large amount of heavy oils, which is abnormal for a plain residual coal tar. Such a product could, however, have been prepared by distilling a mixture of coal tar and water gas tar and this would seem to be the most probable assumption, in view of the rather high percentage of light oils which are free from naphthalene and the presence of considerable quantities of naphthalene in the heavy oils. Had no light oils been present and the heavy oils been free from naphthalene, it would have shown the properties of a true cut-back coal tar, the percentage of free carbon eliminating any possibility of its being a straight residual water gas tar. This tar does not contain an excessive amount of free carbon and when heated is suitable for use as a semipermanent binder in the surface treatment of macadam roads. Owing to its fluidity it is not suited for macadam construction.

Tar No. 2 might be employed in construction work but contains more free carbon than is desirable and too small a proportion of heavy oils to the pitch residue for a material of such a low melting point. A tar of this nature is apt to become brittle and dead quite rapidly after application.

Tar No. 3 is somewhat better adapted for road work but contains what should probably be the maximum allowable limit of free carbon and decidedly more naphthalene than is to be

desired. On the whole, however, it may be considered as a fair road binder, the proportion of heavy oils to pitch residue being about normal for a tar of its consistency. This material was prepared by distilling a mixture of crude high carbon coal tar and water gas tar for the purpose of reducing the free carbon to at least 20 per cent. From the analysis of a material of this nature it is rather difficult to tell whether it is a simple residual medium temperature coal tar or a blended tar, but this is not a very important matter, as a knowledge of the properties of the tar itself is of more interest to the road engineer than the method of manufacture. From the experience of the author it would seem quite probable that originally undesirable coal tars may be blended with water gas tars to produce fairly satisfactory residual products.

Blown Tars. — Quite recently residual tars which have been blown during the process of distillation in a manner similar to that described under blown oils (see page 158) have appeared on the market, and in some respects would seem to be preferable to the unblown tars. Contrary to what might be expected from the effect of blowing air through hot oils, the ductility of tars does not seem to be injured by this process, but rather increased. Just what chemical reactions take place is not known, but they are probably similar in character to those which occur upon blowing oils, although in this case the aromatic compounds are condensed and oxidized in place of the polymethylenes. One effect of blowing seems to be a raising of the boiling points of some of the hydrocarbons, which increases the pitch contents. This is indicated by the results, shown in the following table, of an examination of two residual water gas tars of approximately the same consistency, one of which was blown during distillation. The two tars referred to are numbered 2 and 3, No. 2 being the blown product. No. 1 is also a blown product but of a more fluid nature.

In all of these products the low carbon content and lustrous fracture of the pitch residue show that they have been prepared from water gas tars. They are all suitable for road

COMPARISON OF BLOWN AND STRAIGHT RESIDUAL WATER GAS TAR.

| | Blown. | | Plain Residual. |
|---|---------------------|-------|--------------------------|
| | ı · | 2 | 3 |
| Character | Smooth, Viscous. | | Smooth, Very Viscous. |
| Specific gravity | 1.158 | 1.167 | 1.165 |
| Water, per cent by vol First light oils to 110° C., per cent by | 0.0 | 0.0 | 0.0 |
| vol | • 4 | 0.5 | 0.0 |
| cent by vol | • 7 | 3.0 | 6.3 |
| by vol | 33.2 | 29.0 | 51.9 |
| by vol | 65.7 | 67.5 | 41.8 |
| | 100.0 | 100.0 | 100.0 |
| Pitch residue (per cent by weight) Free carbon | 69.4 | 71.2 | 45·4 2·53% |

Remarks.—None of the distillates showed more than a trace of precipitated naphthalene when cold and all of the pitch residues had a lustrous fracture.

construction, but No. 3 has an almost abnormally low pitch residue, which is characteristic of straight distilled water gas tars. This property has been greatly modified by blowing, as shown by Nos. 1 and 2. Blown tars have not, however, been in use for a sufficiently long time to warrant any very definite assertion as to their lasting qualities.

Summary and Conclusions. — In this chapter the characteristics of various tars with relation to the treatment of roads have been discussed at some length, and the methods of preparing them described. Our present knowledge of the effect of composition upon the physical properties of tars is somewhat limited and much yet remains to be investigated. The foregoing should, however, serve as a working basis for future investigations and will, it is hoped, prove of some service in enabling the road engineer to form a correct idea of the properties most

essential in tars that are to be used as dust preventives and road binders. It is probable that the near future will see an immense amount of road work in which tar is employed as a binding medium. The possible available supply of tar in this country is quite as great as that of good road oils and there seems to be no reason why both classes of binders should not continue to compete on an equal footing. As compared with good road oils the good road tars may perhaps tend to weather a little faster and are certainly somewhat more susceptible to temperature changes. They are on the other hand much more powerful binders than oils on a basis of like consistency and should if properly selected and used give fully as satisfactory results.

CHAPTER XII.

THE APPLICATION OF TAR AND CONSTRUCTION OF BITUMINOUS MACADAM.

THE earliest recorded attempt to use tar as a road binder was made at Nottingham, England, about 1840, in the construction of a tar macadam road, and soon after this at Sheffield, in a similar manner. In 1854 its use in this connection was introduced in Paris and in 1866 in Knoxville, Tennessee. In 1867 the application of tar in the surface treatment of roads first suggested itself to French engineers and from then until 1903 a number of isolated experiments were conducted along this line in France, England, Australia, Italy and the United States. Since 1903 the subject has received more general attention and particularly during the last few years. While the surface treatment of roads with tar was undergoing a slow process of development, its use in street paving suddenly came into prominence in 1871 at Washington, D. C., fostered under patents granted to Snow and Davis. In these patents sulphuric acid was employed as a hardening agent, and a variety of materials, such as sawdust, ashes, etc., were used in the mixture. During the next seven years about 750,000 square yards of tar concrete pavement were laid in this city. Owing to the fact that but little attention was paid to the character of the tar employed, and very probably to the use of sulphuric acid, many of these pavements failed within a few years and had to be relaid. These failures proved to be a severe setback to the use of tar as a paving material in this country, as the work at Washington attracted quite general attention. Incidentally they also proved a boon to those interested in the asphalt industry, who by discrediting tar advertised their own products to advantage. While the author does not wish to compare

these two substances as paving materials, he believes that the general discredit thrown upon tar because of its early failures is greatly retarding its use in this country in modern road construction. In spite of its many failures and the fact that the work at Washington was done so long ago that since then many asphalt pavements have been laid, worn out and relaid a number of times, a few of the original tar concrete surfaces still remain intact as a witness to the possibilities of this material. Ouite recently a number of sections from one of these pavements which had been down for over 34 years were cut out under the author's supervision, for the purpose of making an examination. Shortly after completion this pavement, with all of the other tar concretes, was covered with a course of asphalt topping which has, however, long since worn away, except near the gutters, thus leaving the original tar pavement exposed. The mineral aggregate was found to be exceedingly well bonded and the binder while hard was by no means dead, a strong odor of coal tar being given off by the freshly turned sections. A sawed section of this pavement is shown



FIG. 24. Section of Old Coal-tar Pavement laid at Washington, D. C., in 1873. Surface in good condition in 1909.

in Fig. 24. The quantity of bitumen present amounted to about 6 per cent of the whole and the mineral aggregate showed the following characteristics for three sections which were examined.

OLD COAL TAR PAVEMENT. WASHINGTON, D.C.

| Sample 1 | No | | • • • • • | | • • • • • • • • • | 1 | 2 | 3 |
|-------------------|---------------------------|---------|--|------|-------------------|---|--|---|
| Mineral Retain | aggregate: ned on 1 in | ch scre | eend on "" 2 2 3 3 4 4 5 5 4 8 8 1 1 2 2 | inch | h} | 6.8% 2.2% 7.3 26.7 18.7 15.1 4.2 6.6 3.3 3.6 2.7 0.9 8.7 | 6.2% 1.3% 5.0 29.6 34.4 12.5 2.7 3.3 2.1 2.8 .9 1.8 0.6 1.0 2.0 | 6.0% 2.8% 3.6 16.6 21.4 16.7 5.1 7.4 4.7 4.6 1.4 1.3 2.5 7.8 |
| | | | | | | 100.0 | 100.0 | 100.0 |
| Per cent | of voids | | | | | 17.0 | 18.5 | 15.0 |

These results are of interest as showing a type of road or pavement in which tar has proved a very satisfactory binder and it is only reasonable to suppose that with proper care in selection and application these roads can be duplicated. Unfortunately no data are to be had in regard to the physical and chemical properties of the binder which was employed in this early work and any examination of this binder as it exists to-day is of little value for the reason that alterations have taken place during the course of time which mask its original characteristics and make it extremely difficult to isolate the bitumen even as it exists at present in the pavement.

In England, France and Canada, the use of coal tar in the treatment and construction of roads has found much more favor than in the United States, and the two first mentioned countries are considerably in advance of us both in regard to total mileage of tar treated roads and in methods of application. To a great extent we have so far only succeeded in repeating their early and more unsuccessful attempts, and while there is much yet to

be learned as to the quality of tar which will produce the most economical and satisfactory results under given conditions, we should at least profit by their improvements in methods of application, which up to the present time have not been generally employed in this country.

Unlike oils, tars have not so far appeared to advantage in the treatment of any but broken stone roads, and their use in this connection only will here be described. It is quite possible that under favorable conditions both earth and gravel roads may be successfully treated with these materials but so little work of this nature has been tried that at present it is impossible to make any definite assertion in regard to the matter. Tar may be employed either in the surface treatment of old macadam roads or in the construction of new roads. In the former case, it may be used either as a dust layer and temporary binder or as a semipermanent binder, depending largely upon its consistency. In road construction it of course plays the part of a permanent binder, and may be employed in a variety of ways, the two most common being known as the penetration method and the mixing method. In the first case application may be made either by hand or by mechanical spreaders and in the latter either hand or mechanical mixing may be resorted to. A third method of construction, known as the Gladwell system, has also been employed to some extent. All of these methods are described below. It may be stated that the methods of construction are equally applicable to oils and for this reason no details of the construction of oil macadam roads were included in Chapter X. A number of patents covering methods of constructing bituminous macadam have been issued by the United States Patent Office and some are now being adjudicated which if upheld may greatly influence the character of future work of this nature. In the following descriptions of methods it has been the aim of the author to include all points which are considered as best practice, without reference to any one individual patent.

Surface Application of the Lighter Tars. — The term lighter

tars as here used refers to both crude and refined products which are sufficiently fluid at ordinary temperatures to be applied by means of a common sprinkling cart. Most crude coal tars are too viscous for this purpose, but crude water gas tar may often be so employed to advantage. This material can be obtained for about 3 cents a gallon, and when applied at the rate of .3 gallon per square yard on an ordinary macadam will successfully lay the dust for some time. The number of applications required during a season will of course depend upon a number of conditions, but under ordinary circumstances a comparatively few will suffice. This material is quite readily absorbed by the road and contains a sufficient amount of pitch to reduce dust formation to a considerable extent. It has a rather objectionable gassy odor, which, however, soon disappears. When used on roads carrying a great amount of fine material, it is sometimes necessary to apply more than .3 gallon per square yard. In a case of this sort the tar does not bind the dust down firmly to the underlying surface, but it holds the particles well together and keeps them from being raised by passing vehicles or winds. Under the action of traffic this loose or floating surface is alternately compacted and broken up, but does not form a disagreeable mud. During rainy weather, in fact, it has been known to produce a compact, uniform surface which appears to advantage in comparison with the surface in dry weather. In localities where it can be readily obtained with but little cost for transportation, it can undoubtedly be used to advantage, and in many cases should successfully compete with other temporary binders.

Mixtures of crude water gas tar and crude coal tar proportioned so as to obtain a maximum amount of pitch base with the minimum degree of fluidity requisite for cold application produce more lasting results, but by far the best of this type of binders are the partially refined water gas tars from which all water and part of their light oils have been removed, or else the partially refined coal tars which have been cut with light oils until sufficiently fluid for this purpose. Such tars are capable of

developing considerable binding value after application and at the same time act as excellent dust preventives. If a large amount of dust is present on the road it should be removed before application, but under ordinary conditions this is not necessary. If the road is fairly free from dust before application, a single treatment with such tars should render it practically dustless for a season unless the traffic is excessive. They will not prevent raveling, however, under heavy traffic, as their binding value is not sufficiently great. The cost of treatment should amount to not over three cents per square yard per annum.

Surface Application of the Heavier Tars. — When crude tars are not sufficiently fluid to apply cold, it is poor economy to attempt to use them, as the cost involved in heating and handling is not commensurate with the results obtained, for reasons mentioned in the preceding chapter. The heavier tars as here considered will include only dehydrated or refined tars of sufficient fluidity to pour from the bung of a barrel, but too viscous to be applied cold to the road surface. Harder materials than this will not be found satisfactory for the surface treatment of old roads, owing to their inability to penetrate the road. Crude tars have sometimes been boiled in kettles at the roadside until all water has been driven off and the product has attained considerable viscosity. This is a slow and tedious operation, however, and there is much danger of the tar frothing up, boiling over and catching fire if the temperature is raised above 90° C. while the water is being driven off.

Experience has shown that in order to get the best results from applications of the heavier tars the road should be free from dust, perfectly dry, and comparatively warm. If dust and other fine material are present the tar will not be properly absorbed by the surface and, owing to a lack of bond, will soon peel and be removed by traffic. For this reason it can be applied successfully to hard surfaces only, such as are presented by well-swept macadam or cement concrete roads. The presence of moisture will also prevent the tar from penetrating the road, and as a cold surface will chill and stiffen the

material it is necessary that all applications be made in dry, warm weather. Before applying the tar the road should be repaired where necessary, in order to secure as smooth and even a surface as possible. If ruts and hollows are present, the tarred road will not only present a poor appearance, but accumulations of water in these depressions will produce rapid disintegration of the tar, followed by its complete removal under the action of traffic. It is desirable that repairs be made for some time previous to the tar application in order to obtain a wellbonded and consolidated surface to start with, for it has been found that fresh patches which have been tarred are not unlikely to ravel if traffic is at all heavy.

The primitive method of application which has been largely employed in this country up to the present time, and formerly in France and England, is as follows: The road surface is first thoroughly swept in order to remove all dust. The hot tar is then spread on and thoroughly broomed in. The road should, if possible, be closed to traffic and the tar allowed to remain untouched for about twelve hours in order to allow it to soak in. At the end of this time, or sooner if necessary, a coat of clean sand or stone chips should be applied to absorb the excess of tar, and the surface should then be rolled several times to bring it to proper condition quickly. The preliminary sweeping of the road is sometimes done by hand, but an ordinary mechanical street sweeper is often to be preferred, as it performs the work more economically and with greater expedition. The tar is heated in an open kettle preferably mounted on wheels and fitted with a portable fire box. It is usually brought to about 100° C. before being spread upon the road, although a lower temperature is sometimes sufficient, and, if the kettle is of the type described above, the tar may be run out upon the road as required by means of a hose, the kettle being kept just in advance of the work, as shown in Fig. 25. By using two kettles the process may be made continuous, one being charged and heated while the other is in use. Kettles holding easily 9 barrels, or about 450 gallons, of tar without

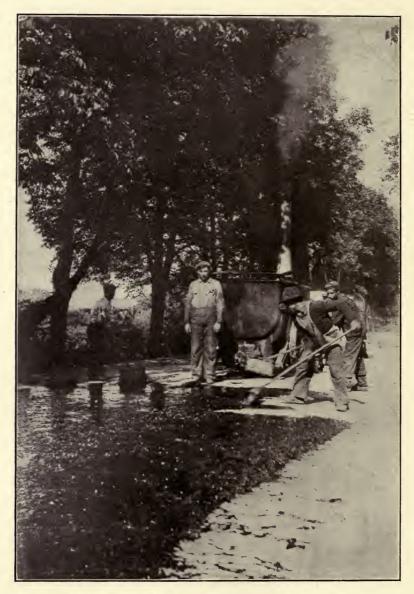
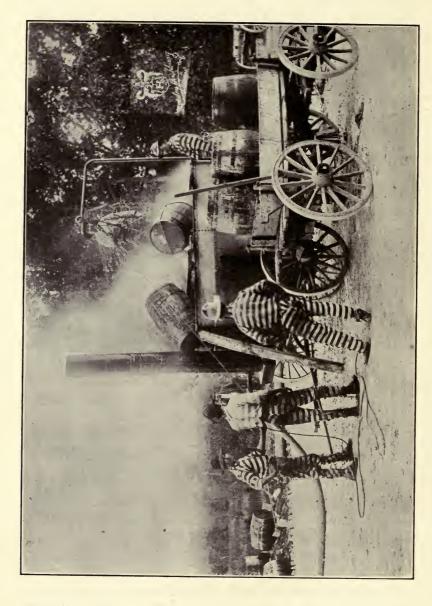


Fig. 25. Application of Tar to Macadam Road Surface.

danger of spilling over, and mounted on comparatively large wheels, are to be preferred for this purpose when long sections of road are to be treated. Fig. 26 shows a type of kettle suitable for this work, and method of loading same. This kettle has a low partition in the center. Cold tar is charged into the section over the fire box and as it becomes heated flows over into the draw-off section so that the operation of loading and unloading may be made continuous. By this means cold tar is prevented from reaching the draw-off. When it is impossible to obtain kettles mounted on wheels, a number of smaller ones holding about two barrels each are sometimes used. These kettles are moved along the side of the road as the work progresses and the hot tar is drawn off into flat-nosed watering-pots, hods, or ladles, and spread by hand. In either case it is necessary to have the hot tar well broomed into the surface to obtain a smooth and uniform coat. This spreading is usually done by laborers with stiff, long-handled brooms, similar to those used in street sweeping, who follow the tar spreaders and broom carefully every portion of road surface. The excess of tar is thus pushed ahead and can be used for covering fresh surfaces.

After the tar has been spread it should be allowed to remain undisturbed for at least twelve hours, as has been stated. In cases, however, where it is impossible to keep traffic away for this length of time, one of two methods may be followed. Either one-half the width of the road may be covered at one time, thus allowing the other half to be open while the first is drying, or a coat of sand or fine stone chips may be applied at once in sufficient quantity to prevent the tar from sticking to the wheels of vehicles. If the first method is followed more lasting results are to be expected, but unless considerable care is taken, the finished road will present a poor appearance, owing to the overlapping of the second application on the first, which produces a seam along the center of the road. More time will also be consumed, as the length of the road will have to be gone over twice. If the second method is employed, there is danger



of the tar being absorbed by the loose material rather than by the road proper, and this will result in a lack of sufficient bond. If the tar is allowed to remain undisturbed for about twelve hours it will, under ordinary conditions, be fairly well absorbed by the road, and then only enough top dressing need be applied to take up the surplus. Either clean coarse sand or one-half inch hard stone chips are to be preferred as a top course, as these afford a harder and better wearing surface than most other materials, such as road dust and gravel. It is customary to finish the road by rolling this fine material into the tar, but when only a light coat is applied the rolling may be unnecessary, as the action of traffic will in a short time produce the same result.

If the tar does not contain much heavy binding material and it is found necessary to patch the road during tarring, the addition of heated pitch, of a consistency similar to that used in road construction, to these patches will better tend to consolidate them and prevent them from being torn up by passing vehicles.

A good tar from which the ammoniacal water, light oils, naphthalene, etc., have been removed and the pitch diluted with a sufficient amount of the heavier tar oils to give it proper consistency will produce the best and most lasting results. There are a number of preparations now on the market which, it is claimed, have these qualities. They should, however, always be examined to see if they are really what they are claimed to be, as the author has examined different lots of some of these preparations and found essential and inexcusable differences to exist.

Owing to the considerable expense and time consumed in applying the tar from kettles, it is advisable to make use of a sprinkling tank. Oil sprinklers such as described in Chapter X have been employed to advantage for this purpose. Mechanical devices for applying the tar under pressure have proven most satisfactory and are now beginning to be adopted in this country. France and England stand foremost in the production of tar spraying machines, having passed through the hand spreading method some time ago.

If the ordinary sprinkler is employed it will be found necessary to broom the tar into the road surface. If, however, the tar is sprayed under sufficient pressure this will not have to be done.

In France a specially constructed sprinkler has been used with some success, which can be manipulated by three men, and which, it is stated, will cover 3000 square meters (3588 yards) of ordinary roadway per day. Tar is pumped into a reservoir, and, after being heated by petroleum in a manner similar to that employed in heating the boiler of a steam-motor car, is sprayed upon the road by means of compressed air contained in an adjoining reservoir under a pressure of 5 kilograms per square centimeter. If the road is first thoroughly swept and all remaining dust removed by means of a vacuum cleaner, the tar is expelled with sufficient force to penetrate well into the macadam, and therefore does not require brooming. A light top dressing of sand should afterwards be applied to the tarred surface.

In England the application of tar by mechanical means has been studied by means of a trial competition, of various machines, carried on by a representative committee of engineers and others interested in road matters. Some exceedingly ingenious devices were produced at this contest, which give promise of good results. A number were designed to carry on the whole operation of tarring at one passage of the vehicle. Some are propelled by steam and so arranged that the road is first swept to remove the dust, which is drawn up by vacuum into a receptacle connected with the machine. The tar is heated and sprayed upon the road under considerable pressure, thoroughly broomed in, and the dust, previously removed, is distributed over the tarred surface.

The first prize winner in this contest is known as the Aitkins pneumatic tar sprayer. During the past year several types of these machines were imported to this country and proved very successful. One of these is shown in Fig. 27.



Fig. 27. Tarspra Machine.

Fig. 28 shows the details of a similar machine described by Aitkin * as follows:

"Mounted on the frame A on the vehicle is a supply tank B to contain the surface-dressing liquid. A receiver C for liquid and air under pressure is placed at the back of the tank and is connected by an inlet pipe D with an air or liquid pump E. pump is operated from a road wheel F by a chain wheel G fixed to the road wheel, which drives through a chain H to a toothed pinion J, actuating the crank shaft K of the pump E. inlet L to the pump is connected with the supply tank B by a tube M, which is conveniently a flexible metallic tube at the tank end, and a rose or strainer N is fixed on the end. An air inlet and regulating valve O is provided on the pipe M between the supply tank and the pump so that either air or liquid may be admitted to the pump, or the proportion of liquid and additional air may be regulated as required for the purpose of agitating and mixing the liquid properly.

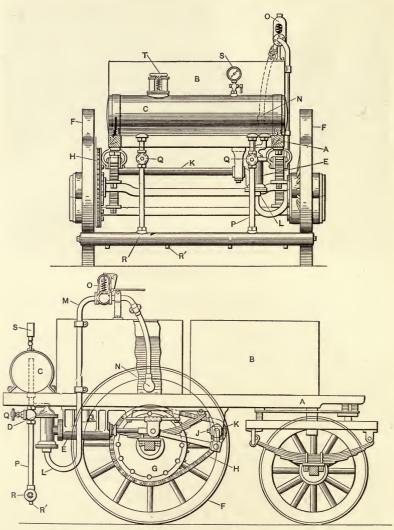


Fig. 28. Sketch of Pneumatic Tar-Spraying Machine.

"Feed pipes P leading from the receiver C and provided with cocks Q conduct the liquid under pressure to a distributing pipe R having jets R' which discharge the liquid onto the road. The distance between the distributing pipe and the surface level of the road may, if desired, be variable to suit the varying pressures in the receiver, the condition of the road, etc. A pressure gage and safety valve T are provided on the receiver C.

"Preferably air is forced into the receiver C from the pump E until the desired pressure of, say, 50 to 100 pounds per square inch is established according to the viscosity of the liquid to be used and other conditions; the strainer N is then introduced into the tank, or connection otherwise made between the tank B and the pump, and liquid is forced into the receiver until the pressure reaches the required degree, say, from 150 to 250 pounds per square inch.

"The apparatus is now ready for work and by opening the supply cocks Q to the distributor R, the liquid is squirted, preferably in the form of fine compact solid streams, of, say, less than one-eighth of an inch in diameter, so as to be of a penetrating character as they are forced directly onto the surface of the road and are also forced into the binding material forming a part of the crust of the metaled surface of the road. The liquid is pumped into the receiver C in a continuous flow and the compressed air originally introduced into the receiver maintains a uniform pressure."

One of the most common faults encountered in the practice of tarring macadam road is failure to remove all dust and loose material from the surface. Too much emphasis cannot be laid upon the necessity for doing this, as the tar will not penetrate through a film of dust, and penetration is essential to success. On an old road places may be found where a considerable amount of fine material is caked to the surface. Such places should be scraped away until the larger stones of the wearing surface are visible. In fact the entire wearing course should be stripped of all fine material until it shows a rather rough but not uneven mass of large stones, thoroughly bedded together but presenting a considerable amount of surface voids. After the tar is spread an excess of stone chips may be applied so that upon rolling all of the surface voids may be filled. The chips thus become firmly bedded in the wearing course and, if those not bound down by the tar are swept from the road, will produce a firm smooth surface.

In order to facilitate penetration of the heavier tars, especially where it is difficult to remove all dust, it will often be found advantageous to first give the road a light sprinkling with a thin, dehydrated water gas tar. This material by oiling the fine particles will help carry the heavier bitumen into the road.

Macadam roads that are treated each season with tar will be found to require less material for each succeeding application. If application is made at the proper rate, the cost of such work should for a period of two or more years prove more economical than ordinary maintenance for a like time. The surface treatment of tar constructed macadam will often prove of value by adding to the life of the old tar matrix. This fact has been recognized in England for a long time. Walker Smith,* in a recent treatise on tar macadam, states that, to his personal knowledge, "tar spraying of surfaces has been carried out for the last twenty years principally in tar macadam back streets and tar macadam footpaths, not as a means of prevention of dust, but in the ordinary way of revivification and repair of a tar macadam surface."

While the repairs necessary on a macadam road are very much lessened by the application of tar, they must not be neglected, for once disintegration begins it spreads very rapidly. Under favorable conditions a surface treated with a heavy tar should last at least one year without requiring repairs. (In many cases, however, it has been noticed that a few months after application the tar disintegrates and rapidly disappears under the action of rain and traffic. A slimy mud is formed in wet

^{* &}quot;Dustless Roads, Tar Macadam." Griffin & Co.

weather which pulverizes into a very fine black irritating dust in dry weather. In such instances the fault would seem to be either in the method of application or in the quality of tar employed. The results described are exactly what might be predicted from the use of a tar prepared at a high temperature and containing a large amount of free carbon and other non-binding material. It is unquestionably the use of such products that has in many cases prejudiced popular opinion against tar as a dust preventive. There is certainly one objection to the tarred road which in most cases is well founded and this is that in frosty weather the road is quite slippery. This fault may, however, be somewhat modified by the character of the top dressing employed, sand and stone chips being preferred to other materials as offering a better purchase to the wheels of vehicles and a better foothold to horses.

The amount of tar required to treat a road will depend upon the fluidity of the material when applied and the absorbing power of the road. Soft rocks, such as limestone and dolomite, will take up more tar than granite or trap and will in general give better results, owing to the greater penetration and consequently stronger bond formed. (According to conditions and method of application, a surface treated road will require from .35 to .70 gallon of tar per square yard when application is made by hand. When applied by machine as little as .21 gallon has been used with good results for a first treatment. In both cases the application of tar must be repeated from time to time but less is required at each successive application.

Decayed vegetation, prolonged rains, and frost are the worst enemies of the tarred road. By keeping the road comparatively free of rotting sticks and leaves, the first trouble may be overcome but the others are not to be avoided. The alternate freezing and thawing of spring, as encountered in some localities, is particularly injurious to a surface tarred road and rapid disintegration of the thin coating is apt to take place even where the surface and subdrainage are of the best. In such localities the road tarred throughout is undoubtedly to be preferred to the

surface treated road, as the latter under the most favorable circumstances is likely to succumb to the attacks of winter and early spring.

The cost of treatment for a road surfaced with hot tar will of course depend upon a number of factors. In France when done by machine it will average about three cents, and when done by hand five cents per square yard. In this country, where it is generally applied by hand, the cost is hardly ever less than six cents and in a great many cases as high as twelve cents and more per square yard. This is largely due to the poor condition of our roads before treatment, which necessitates the application of more tar and more surface dressing than if they were in good condition in the first place. In England it is claimed that the pneumatic tar sprayer will apply the tar at a cost of about \$5 per mile of eighteen feet roadway, exclusive of the cost of the tar. It is very doubtful if the expenditure of over five cents per square yard for the surface treatment of any road with tar will prove good economy in the long run. Resurfacing or reconstruction with a tar matrix is much the better practice, although the first cost is somewhat higher. The price of refined tar for surface treatment will in this country run from five to eight cents at the present time.

Application of Tar to Cement Concrete Road Surface. — Before leaving the subject of surface treatment, mention should be made of an experiment conducted by Mr. Charles W. Ross, at Newton, Mass., in 1908, in which tar was used in the treatment of a cement concrete road surface which had begun to show signs of scaling off under the action of traffic. To quote from a paper by Mr. Ross: * "The experiment was tried by putting a coat of Tarvia A, also a preparation of coal tar just as it was taken from the gas works. This was heated to a temperature of about 180 degrees and spread onto the surface of the cement, swept down evenly with a broom and then a light coating of stone screenings or fine screened gravel applied, which I think I much prefer to the stone screenings.

^{* &}quot;Concrete Roadways," Good Roads Magazine, May, 1909, p. 142.

"The surface has been kept intact for over a year and the tar preparation on the surface is in good condition at the present time."

Bituminous Macadam Construction, Penetration Method. — The penetration method may be employed in the construction of oil macadam in the same manner as for tar macadam. There are a number of variations to this method as practiced by different road engineers, but in general it may be described as follows:

The roadbed is first graded, shaped and rolled as in ordinary macadam work. A course of number one crushed stone, ranging in size from approximately one and one-quarter to two and one-half inches, is laid loose to a depth of five or six inches, and thoroughly rolled, sand or stone screenings being applied in sufficient quantity to produce a firm sound surface. There should be no excess of fine material, however, and the tops of the large stone should always be visible. With the exception of being somewhat rough, this course is practically a finished road but is intended only as the foundation for the bituminous concrete which is afterwards formed. Water may be used in the construction of the foundation if desired, but this is seldom deemed necessary. The filler of fine material serves two purposes. It makes the foundation solid and cuts off the flow of any bitumen, which is later applied, from the base of the road, where it is not needed. A somewhat rough surface is desirable in order that the upper course may key in. Any excess of screenings is, therefore, to be avoided, as the presence of too much fine material will prevent the formation of a good bond between the two courses.

The second course of crushed stone, ranging in size from one-half inch to one and one-quarter inch, is laid on the foundation course to the depth of two and one-half inches and well rolled. Where the roadstone is soft, larger sizes may sometimes be employed to advantage, as noted in Chapter I. A light coating of clean one-half inch stone chips free from dust is then applied and rolled into the surface which should, however, never be

completely filled. Tar or oil heated to a considerable degree of fluidity is next poured or sprinkled over the road at the rate of from one to one and one-half gallons per square vard. This is allowed to penetrate into the wearing surface and should completely cover the upper two inches of stone. Clean stone chips are next applied and the road again rolled, care being taken not to run the roller too fast nor to reverse it suddenly on the bitumen coated surface. At this point the surface may wave somewhat under the roller, owing to the at first slightly lubricating effect of the bitumen. the screenings have been rolled, in all surplus of fine material is swept to the sides of the road for future use. A seal or flush coat of hot bitumen is then sprinkled or painted on the surface at the rate of from 0.3 to 0.5 gallon per square yard, after which sufficient stone screenings, running from one-half inch to dust, are applied to fill the surface voids and take up any excess of bitumen. The screenings which have been previously swept from the surface may be used for this purpose. The road is completed by a final rolling, but should preferably not be opened to traffic for a few days or until the green bitumen has had a chance to come to a sort of set. In this work excessive rolling should be avoided before applying the bitumen, as too free a use of the roller causes the stones to become rounded and covered with dust, thus preventing proper interlocking of the individual fragments with one another, as well as good adhesion of the bitumen to the stone surfaces.

The hot bitumen may be applied either by hand, directly from portable tar kettles or by means of sprinklers as described under the surface treatment of roads. Two types of portable kettles suitable for this work are shown in Figs. 26 and 29.

Fig. 26 has already been described. In Fig. 29 is shown an asphaltic oil heating truck. "The body, or fire box of the truck, as well as the tank, is made of the best grade No. 8 sheet steel. The tank is built separate from the body or fire box of the truck, and in the event of the tank becoming burned or otherwise damaged, it can easily be removed from the setting

and be repaired. The furnace is made in box form of steel plates, the sides being reinforced. The truck is mounted on four wheels of large diameter and broad tread.

"An arrangement of a rack of light construction is provided on the top of the kettle for carrying three barrels of material. This rack is covered by a galvanized iron hood of light construction for the purpose of retaining the heat arising from the

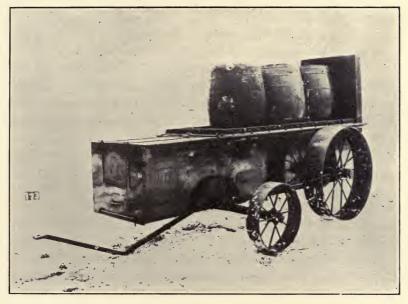


Fig. 29. Asphaltic Oil Heating Truck (Iroquois Iron Works).

setting and utilizing it for heating the barrels of material carried on the rack. The hood is provided with three handles on either side, rendering it easily removed.

"This kettle is so designed that it can be operated with equally good results by the burning of oil or wood. For the burning of oil there is arranged on the front of the machine a fuel tank having a capacity of thirty gallons. Three oil burners and the necessary piping, air compressor, pressure gauge, valves, shut-off cocks, etc., are all arranged as a unit, which may be

easily detached. When wood is desired as the fuel, the unit can readily be removed and substituted with a solid door furnished with the truck.

"For the easy handling of barrels of material from the ground, steel skids are provided, arranged to hook over the end framing, directly over the fuel tank; when not in use they can be hung on hooks, on the side of the fire box, provided for the purpose.

"The kettle is equipped with a 3-inch pipe and draw-off cock, arranged in a straight line, so that should the asphaltic oil become congealed, the piping and draw-off can be readily cleaned with a rod which is provided for that purpose."

A very good arrangement for distributing the bitumen when kettles of this sort are used is to connect a heavy rubber hose carrying a fan shaped copper nozzle to the draw-off. This nozzle should be about 12 inches in length and fitted with a slot one-eighth inch wide. When applying the tar it is worked backward and forward across the entire width of the road and only a few inches from the surface, the direction of the slot being parallel to the length of the road. By this means a fairly uniform distribution may be secured with a little practice, with slight chance of the bitumen cooling to any extent before coming in contact with the roadstone. In order to avoid disturbing the upper course of stone while the tar is being applied, it is sometimes advisable to finish only one-half the width at a time. In the treatment of the first half the wearing course is laid from one gutter to only a little beyond the center of the road. The heating kettle is then moved along the foundation course and the bitumen applied to the opposite side by means of the long hose and fan shaped nozzle before described. After one-half of the width is finished the wearing course may be laid on the other side so as to produce a feather edge joint along the center, and application made in the same manner, by moving the kettle along the finished section. If a mechanical sprinkler or spraying cart is used, it will be found necessary to run it over the unbounded wearing course, in which case it will rut the surface and if

horse drawn will tear it up badly. After the bitumen is applied these inequalities are difficult to obliterate and an uneven surface is likely to be produced if particular attention is not paid to raking the loose stone into place and rolling carefully.

The object of the penetration method is to produce a bituminous concrete wearing surface without depending upon labor or machinery for mixing. As has been stated, an attempt is made to cover the upper two inches of stone. While the whole surface may be covered with comparatively little bitumen, a uniform penetration for the depth of two inches cannot be secured with less than one gallon of bitumen per square yard. This will amount to approximately a 6 per cent mixture, which is about right for bituminous macadam construction. If lasting results are to be expected, no smaller quantity should be applied. The seal coat of approximately 0.5 gallon of bitumen to the square yard is very desirable, as it protects the underlying thinner films from weathering and disintegrating. In some cases attempts have been made to construct a macadam road according to this method with only a little over 0.5 gallon of bitumen per square yard all told. This amounts to nothing more than a surface treatment and the bitumen can, therefore, only be expected to serve in the capacity of a semipermanent binder. Roads so constructed will usually require additional treatment at the beginning of the next season.

The main disadvantages of the penetration method of construction are (1) the uncertainty of obtaining a uniform distribution of bitumen throughout the wearing surface, (2) lack of uniformity of the mineral aggregate and (3) necessity of employing a binder of softer consistency and lower mechanical stability than is desirable for a permanent matrix. The first objection is probably the most serious. No matter how much care is taken in application, it is impossible to be certain that a uniform distribution has been secured. Small channels in the wearing course are likely to drain the hot bitumen away from certain portions and tend to concentrate it in others. A patch of dust here and there or a few damp stones may completely

prevent absorption at these points. Moreover, if the surface is a trifle too cold or the bitumen not quite hot enough, when it strikes the road, penetration may be almost completely cut off by the binder congealing and sealing the surface. All of this, while not very apparent at first, is apt to show up as the road is subjected to traffic. Soft wavy places may develop where the bitumen has become concentrated and other places may ravel out where there is a lack of binder. If a thick coat of bitumen has congealed on the surface, the road will become soft and sticky in warm weather and in cold weather is likely to pick up and peel off under the action of traffic.

Lack of uniformity in the mineral aggregate, except as it affects the distribution of the binder, probably produces no more serious results than in ordinary macadam construction. Uniformity is, however, a most desirable feature and can be much better controlled in the mixing method which will be described later. While it is necessary to employ a binder of sufficiently soft consistency not to congeal immediately upon coming in contact with the roadstone under normal conditions, and while such materials are perhaps necessarily deficient in binding value for construction work, it is possible by proper selection to obtain one which will have the property of attaining the desired consistency after application. Cut-back oil or tar products which hold a certain amount of readily volatile constituents are best suited for this kind of work. As a rule they should have sufficient original consistency to barely flow when cold, or otherwise the road surface will be soft and wavy for some time after application.

In spite of the objections which have been advanced against the penetration method, it has the advantage of being cheap, and under favorable conditions of producing a very satisfactory road for traffic which is not excessive. If the binder is applied in warm dry weather during the heat of the day, it is often possible, although never absolutely certain, to obtain a surprisingly uniform distribution, and in a number of instances which have come under the author's notice, upon digging into the road surface at

almost any point, the stone fragments have been found to be exceedingly well coated. Work of this nature should cost but a few cents per square yard plus the price of one and one-half to two gallons of binder over that of ordinary macadam, as the labor of applying the binder is small, providing that suitable heating and spreading devices are employed, and the very considerable cost of watering made necessary in regular macadam construction is entirely eliminated. In many cases, however, the cost of such work has been excessive owing to makeshift apparatus employed, which requires much labor to operate and many costly delays through breakage and inefficiency. Now that suitable heating and spreading devices can be purchased in this country, it will prove extremely poor economy to attempt to work with inferior appliances, not only because of greater labor costs, but also unsatisfactory results which are more than likely to follow the use of crude apparatus.

Before leaving the penetration method, mention should be made of the so-called bituminous sand filled macadam which has been advocated by some. This type of road is quite similar to that already described, but certain modifications are made which allow the use of a more fluid bituminous binder. Upon the foundation course prepared in the usual manner a four inch layer of crushed stone ranging from one-half to one and onequarter inch in size is laid and thoroughly rolled. A filler of sharp clean sand or stone chips free from dust and not larger than one-quarter inch is then applied and rolled into the road. A number of light applications should be made until the road will take up no more. All excess is then swept from the surface and the heated bitumen applied at the rate of approximately one gallon per square yard. As the voids in the wearing course have been fairly well filled by the sand or stone chips, it is necessary to employ a binder which is quite fluid at ordinary temperatures in order that a good penetration may be secured. This is also allowable as the mineral aggregate has greater mechanical stability than in the regular penetration method.

After the binder has been absorbed by the road surface, which may take from three to seven hours, a light coat of clean one-half inch stone chips is applied and rolled into the surface voids. A paint coat of hot bitumen at the rate of approximately one-half gallon per square yard is next applied and the road finished by rolling in sufficient screenings to take up all excess of bitumen. Roads, so constructed are fairly well adapted to withstand moderately heavy mixed traffic.

Resurfacing, Penetration Method. — The penetration method may be followed when resurfacing old macadam roads as well as when constructing new roads. In such cases the old surface should be spiked up or scarified and brought to even crown and grade by the addition of fresh stone where necessary. It is then rolled until firm, after which it is made to serve as a foundation for the wearing course, which is laid and treated with bitumen in exactly the same manner as described for construction work. If it is desired to apply less than two inches of fresh stone, the foundation should be well harrowed before rolling in order to work the very fine material of the old surface further into the body of the road and thus allow a deeper penetration of the bitumen.

Bituminous Macadam Construction, Mixing Method. — The construction of bituminous macadam according to the mixing method is identical with the penetration method up to the completion of the foundation course. The wearing course, which is usually laid to a finished depth of two or two and one-half inches, is composed of a more or less carefully graded mineral aggregate which has been previously mixed and coated with a hot bituminous binder. Sometimes the aggregate itself is heated before mixing and sometimes used cold. In the former case a binder of high original consistency may be employed, while in the latter it should have about the same properties as one which is to be used according to the penetration method. For a number of reasons the heated aggregate is to be preferred. The mixture may be made either by manual labor or by machinery, as described below.

After the bitumen coated stone has been laid to the desired depth it is rolled either with or without the addition of one-half inch stone chips free from dust. Where the latter can be done without the stone sticking to the roller wheels a very satisfactory surface may be secured by the application of a light coating of bitumen covered sand or stone chips which is rolled into the surface voids and dusted over with stone dust or cement. In the former case all surplus of screenings should be broomed off and a flush or paint coat of bitumen applied at the rate of from 0.3 to 0.5 gallon per square yard, after which screenings are again applied and rolled down in sufficient quantity to take up the excess of bitumen.

Theoretically, in order to acquire the maximum degree of stability the mineral aggregate should be so graded that if a given space is filled with the largest size fragments, the other sizes will be so proportioned that the next smaller will occupy only the voids between the first size, the next smaller the remaining voids and so on down to an impalpable powder. While particular attention is paid to the grading of a sheet asphalt topping and also to the wearing course of the type of pavement known as bitulithic, such refinement is far too expensive for ordinary country highway construction and for the most part unnecessary. Bitulithic, because of its high cost at the present time, may be classed as a city pavement. Where less refined methods of grading and mixing the aggregate are followed good results may be obtained in the construction of country and suburban highways at a very much lower cost. Other things being equal, dense surface mixtures containing a minimum percentage of voids are to be preferred to those having a higher percentage of voids. Maximum inherent stability or capacity for resistance to displacement of the individual constituents of an aggregate is not only dependent upon the proportion and arrangement of these constituents but also upon the size of the largest fragments. This fact has been recognized for a long time and has undoubtedly governed the construction not only of bituminous macadam roads, but of ordinary macadam as well.

remained, however, for Frederick J. Warren to state in a very broad way the size and proportions of the constituents of a mineral aggregate which should possess inherent stability. In 1901 he was granted a patent * covering a combination of graded broken stone and dust of different sizes, so proportioned that the whole should have a very low percentage of voids, and mixed with about 6 per cent of a bituminous cement. In this patent the sizes of stone are stated in the following proportions:

| Broken stone from $3''$ to $\frac{1}{2}''$ | 70 parts |
|--|----------|
| Broken stone from $\frac{1}{2}$ " to $\frac{1}{10}$ " | 20 " |
| Broken stone from $\frac{1}{10}$ " to $\frac{1}{40}$ " | 20 " |
| Broken stone from $\frac{1}{40}$ " to $\frac{1}{80}$ " | 4 " |
| Dust less than $\frac{1}{80}$ " to $\frac{1}{200}$ " | 3 " |
| Dust less than $\frac{1}{200}$ " | ı " |

In 1903 Warren was granted another patent † covering the use of a mineral aggregate, in combination with a bituminous binder, proportioned as follows:

| From $3''$ to $\frac{1}{4}''$ | 50 to 80% |
|---|-----------|
| From $\frac{1}{4}$ " to impalpable powder | 10 to 49% |
| Impalpable powder | I to 3% |

His idea was that mineral aggregate so proportioned would possess sufficient inherent stability to make it possible to employ a very much more fluid binder than in the case of sheet asphalt topping, where all of the constituents are of small size. While the larger size fragments are desirable on this account too large a maximum is apt to produce a surface mixture which will wear unevenly under traffic. It is probable that the use of stone which will pass a two inch ring will in practice prove the best maximum to adopt, except in the case of soft rock. The old coal tar pavement mentioned at the beginning of this chapter may be considered as a good example of this type.

In country road work it is for the most part impracticable to carefully grade and proportion the various sizes of stone. For reasons of economy it is often necessary to make use of the

^{*} U. S. Patent, 675, 430. † U. S. Patent, 727, 505.

entire crusher run of material, and the crusher run is at best separated into three or four sizes. For ordinary purposes a roughly graded aggregate composed of a mixture of two or three of these sizes can be made to give satisfactory results. Thus, for a rock that produces comparatively little dust upon being crushed, a mixture of twenty-seven parts by weight of stone one and one-half to three-fourths inches in size to ten parts of screenings three-fourths inch to dust has been found to produce a very satisfactory mixture. Where the dust is excessive, screenings free from dust may be used and a small amount of dust afterwards added.

As in cement concrete work it will prove an excellent plan to make up trial batches before work is commenced in order to determine the densest practicable mixture. This can be done by making two cubical boxes, one to hold an even cubic foot of material and the other with a capacity of six cubic feet. A total of six cubic feet of material may be measured out in any desired proportion by means of the smaller box, and thoroughly mixed. The mixture is then placed in the larger box, struck level and its depth noted. That mixture showing the lowest depth will be the densest. It is probable, however, that in no case should the amount of crushed stone larger than one-half inch screenings be less than the screenings and dust combined.

Resurfacing, Mixing Method. — The mixing method may be employed in resurfacing old roads as well as in constructing new ones. For this work the old road should be spiked up and recrowned in the same manner as described under resurfacing according to the penetration method. The presence of an excessive amount of fine material on the surface of the foundation course thus prepared should be particularly guarded against in order that the wearing course shall not be prevented from keying into the stone below. The wearing course may then be prepared, laid and finished off in exactly the same manner as for construction work.

Hand Mixing. — While mixing machinery is unquestionably to be preferred in carrying on extensive work, it may some-

times be desired to construct short sections of road where the use of such machinery will not prove economical. In a recent article * the author has described a method of hand mixing bituminous concrete for road work, which he has himself used, and this description is here included for the use of those who desire to do similar work. The method was employed by the Office of Public Roads in coöperation with Mr. Charles W. Ross, Street Commissioner of Newton, Massachusetts, during the summer of 1908.

It may first be stated that if such work is to be conducted upon an economical basis, the most essential factor to be considered is the proper arrangement and control of labor. Under ordinary conditions the construction of a bituminous macadam road represents the combined labor of three working units, which may be called the mixing force, the teaming force and the construction force. As it is of course necessary that some material be mixed before the construction force can begin to lay the bitumen coated material, and as in many instances it is preferable to carry on the mixing operation near the source of stone supply, it is evident that these three units should begin work at different hours, in order that they may all be kept constantly employed. In other words, the mixing force should begin work at an earlier hour than the teaming force and, depending upon the length of haul, the teaming force should begin work at an earlier hour than the construction force.

With this understanding we may eliminate the two latter and consider only the mixing force. In the work at Newton the following method of procedure was evolved and proved satisfactory in regard to both efficiency and economy:

The mixing plant was located quite close to the crushing plant, as shown in Fig. 30. The working force consisted of 1 foreman, 15 laborers, and 1 single team, and the apparatus of 2 two-barrel heating kettles, 3 stone heaters, 2 stone gauges, 1 mixing platform, 12 long handled shovels, 2 iron rakes, and 1

^{* &}quot;Hand Mixing for Bituminous Macadam Construction," Good Roads Magazine, September, 1909.

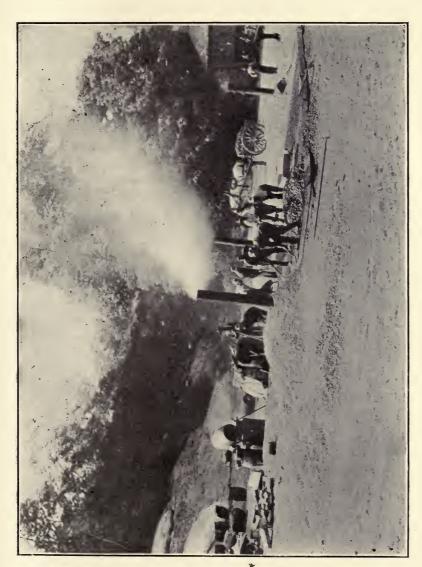


Fig. 30. Hand Mixing Plant for Preparing Bituminous Concrete.

long handled one-gallon bitumen ladle. Wood was employed for fuel. With this equipment it was found possible to prepare under favorable conditions 37 cubic yards of a dense, evenly coated mineral aggregate per day of eight working hours. The detailed cost data is given in the table below.

The mixing platform measured approximately 20 feet in width by 30 feet in length and was made by laying 2-inch planks side by side and as close together as possible upon a level piece of ground. The stone heaters were semicylindrical in shape and measured 8 feet in length, 4 feet 6 inches in width, and 18 inches in height. They were constructed of five-sixteenth-inch boiler iron with three inside lateral braces and closed at one end. At the closed end of each heater was fitted a 6-foot smoke stack 12 inches in diameter. These three heaters were arranged about the platform as shown in the illustration. The stone gauges were of the ordinary bottomless box type fitted with handles. The one for gauging the small stone, which ran from three-fourths inch to dust just as it came from the crusher, held when level full about 350 pounds of stone. The other, for gauging the larger stone, running from one and onehalf inch to three-fourths inch, held about 960 pounds of stone. One gauge of each size combined was found to be a very satisfactory quantity for four men to mix at one time. The two side heaters were employed for heating the large stone, the end heater for the small stone.

It was found most convenient to mix two batches of stone at the same time, the arrangement of labor and *modus operandi* being as follows. The single team kept the stone pile beside each heater constantly replenished and at intervals assisted in hauling the bituminous mixture to the road. One laborer was detailed to attend to the heating kettles and began work 30 minutes earlier than the rest of the force, in order to have a supply of hot bitumen ready at the start. As required, two men from the rest of the force assisted in rolling the barrels of bitumen upon barrel platforms, from which they could be emptied into the kettle not in use. In this way all delay in

waiting for the bitumen to be heated was avoided. The foreman directed the work of mixing and measuring out the hot bitumen. At each heater two men were employed in heating the stone which they took from the pile nearby. With a bitumen of such consistency that at ordinary summer temperature it would drain slowly from the bung of the barrel, it was found that with a good fire beneath the heater the stone would become sufficiently warm for mixing in a very short time. The operation of loading and unloading the heaters was, therefore, almost continuous.

Four laborers were employed in mixing each batch of stone. The small gauge was first placed near the rear of the platform and at an equal distance from the rear heater and one of the side heaters, and was filled with the hot fine stone from the rear heater. It was then removed to a similar position on the other side of the platform for measuring the second batch. The pile of stone so deposited was flattened out so that the large gauge could be placed upon it, and this gauge was filled with large stone from the nearest side heater. It was then used in a similar manner for the second batch of stone, which was prepared in exactly the same way. At this point the foreman spread four gallons of hot bitumen upon the prepared pile of stone, and three laborers immediately began to turn it over from the bottom with shovels, working the pile toward the front of the platform. A fourth laborer raked the turned pile as it was being formed. After the first turning two more gallons of hot bitumen were applied by the foreman and the pile again turned and raked in the same manner as before, thus bringing the mixture to the front of the platform, where it was ready to be loaded upon the wagon to be carried to the road. This operation was at the same time being repeated by another set of men on the other side of the platform.

When prepared in the manner described, two turnings were sufficient to secure a uniform mixture in which each fragment of stone was thoroughly coated with bitumen. It was found that if the fine material was not placed at the bottom of the pile before mixing, from four to six turnings were required in order to

secure a uniform mixture. This was due to the fact that if the fine stone was coated first, so much bitumen was absorbed that it was a difficult matter to get the larger particles covered. In order to avoid loss of time at the construction end of the work, one man from each mixing gang assisted the teamsters in loading the mixture upon the wagons as occasion arose.

It was found that this mixture was so dense that it compacted but little under the roller, so that where a two inch course of bitumen-covered stone was desired upon the ordinary foundation course, I cubic yard would cover practically eighteen square yards of road. Work so conducted showed the following cost for mixing. Interest on capital invested for and loss for depreciation of apparatus are included. Allowance for delays because of rainy weather should also be made, but as this is an uncertain factor it is not considered in the table of cost.

COST DATA OF HAND MIXING.

| | Per Day. | Per Sq. Yard. |
|--|---|--|
| r foreman at \$2.50 | \$ 2.50 30.00 3.50 2.00 .40 | Cents. .38 4.51 .53 .30 .06 |
| Depreciation of apparatus at 12 per cent per annum Total | \$38.53 | 5.80 |
| Bitumen in mixtureBitumen painted on road surface | | Per Square Yard. o.8 gal5 gal. 1.3 gal. |

When the mixing method is employed the cost of watering should be deducted in order to ascertain the excess cost over the ordinary form of macadam construction. Best practise, on the other hand, requires that a coat of hot bitumen be painted upon the rolled course of bitumen covered stone, and the labor thus entailed has been allowed to offset the cost of watering in obtaining the final excess cost. As the cost of various bituminous binders also differs greatly, only the approximate quantity required is given in the above table. From these figures, however, it is seen that under favorable conditions a macadam road constructed with a two inch top course of bitumen-covered stone should not cost over six cents per square yard plus the cost of 1.3 gallon of bitumen delivered, over and above the cost of an ordinary macadam road of the same depth.

A better type of heating kettle, for such work, than those described above is shown in Fig. 29.

Mechanical Mixing. — There are a number of excellent portable mixers manufactured in this country for preparing bituminous concrete, and their use is certainly to be advocated where long stretches of bituminous macadam roads are to be constructed. Some of these mixers are very complete, being equipped to heat both stone and bitumen and automatically proportion and mix the concrete. Ordinary cement concrete mixers are hardly suited for preparing bituminous concrete, although they are sometimes employed for this purpose. asphalt mixer of the type shown in Fig. 31 is to be greatly preferred. This mixer is equipped with a double set of revolving blades inclined to the right and left, which arrangement has proved the most successful for turning out a well coated uniform concrete at a rapid rate. These blades are so set upon the shafts that the mixture is continually tossed upward and at the same time worked toward the center. The lever operates to open a slide in the bottom of the mixer through which the concrete is discharged.

In Fig. 32 is shown a modern auto-portable paving plant well equipped to turn out bituminous concrete for road work. A twenty horsepower steam boiler supplies power to both move the machine and operate the entire plant. This plant consists of a drying cylinder; a furnace to heat the cylinder and melt the bituminous cement; a heating tank located above the furnace and

capable of holding 300 gallons of bitumen; an automatic measuring device for proportioning both the bitumen and aggregate; a mixer under which is located a small furnace for maintaining a uniform temperature during the mixing process; and a dust collector. The drying cylinder is three feet in diameter by eighteen feet in length, and is so constructed that the mineral aggregate is moved steadily forward toward the dumping end, meanwhile being subjected to an even degree of heat which thoroughly

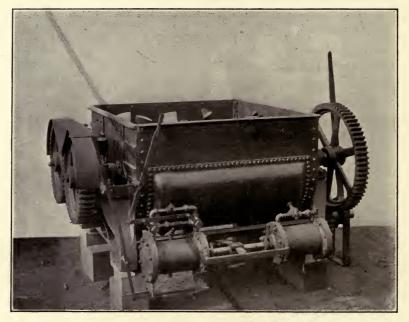


FIG. 31. Asphalt Concrete Mixer (Iroquois Iron Works).

dries and heats it so that it can be readily mixed with the hot bitumen. The automatic measuring device regulates the amount of aggregate that goes into the mixer and is divided into two compartments so that one can be filling while the other discharges. This device is connected with measuring pots located on the side of the tank containing the bitumen and whenever the mineral aggregate is discharged into the mixer, one of the

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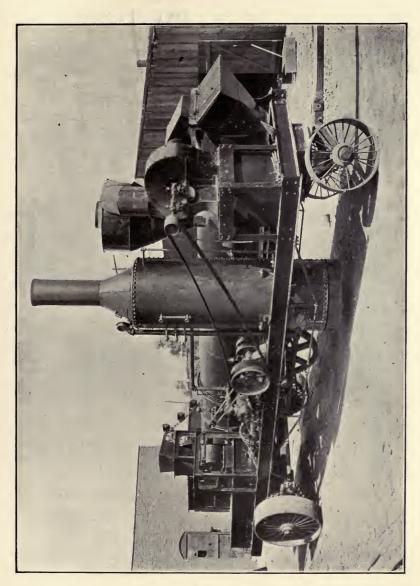


FIG. 32. Auto-Portable Paving Plant (The American Paving and Manufacturing Co.),

measuring pots automatically opens and discharges its contents into the mixer at the same time. The plant is self-propelling and is arranged so that each part may be operated independently. Its weight is approximately nine tons. It measures twenty-nine feet in length, ten feet in width and ten feet in height. Its capacity is from forty-five to fifty-five cubic yards per day, being equivalent to the work of about twenty men. This plant can be operated directly on the road and the hot concrete laid as soon as it leaves the mixer.

In cases where an asphaltic cement has to be handled upon the road it will often be found convenient and expeditious to make

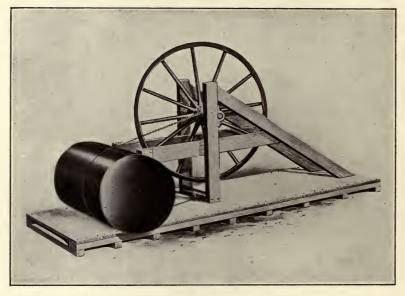


Fig. 33. Asphalt Cutter (Standard Asphalt and Rubber Co.).

use of an asphalt cutter, such as shown in Fig. 33, for cutting the cement into chunks before placing it in the heater. The principle of this machine is made apparent in the figure and requires no description other than to state that the asphalt is cut by means of a wire.

In some instances the road engineer may desire to prepare a



Fig. 34. Portable Asphalt-Oil Mixing Plant.

bituminous binder which will possess certain properties not obtainable in any trade products. To meet this need portable asphalt-oil mixing plants have been devised for the purpose of preparing any desired mixture of solid bitumen and flux. Such a machine, designed by Mr. J. C. Travilla, Street Commissioner of St. Louis, is shown in Fig. 34.

"The plant consists of a melting and agitation kettle, air

pressure for furnishing compressed air for agitating the oil asphalt compound and for forcing it from the melting kettle to a distributing wagon, a steam pump as an auxiliary for pumping heavy oil from the tank car to the melting kettle and a steam boiler for the operation of the air pressure and steam pumps. The kettle has a capacity of 1350 gallons, is divided transversely into two equal parts, one compartment being intended for melting and mixing the oil-asphalt and the other for agitating the oil-asphalt by means of air blown into the contents of the kettle under low pressure." This plant is not only useful for preparing heavy products for construction work, but also for reinforcing the lighter road oils with asphalt to any desired consistency and binding value.

Bituminous Macadam, Gladwell Method. — In 1906 a method of resurfacing and constructing macadam roads with the use of a matrix of tar and sand or stone chips as a binder was developed in England by Gladwell and Manning. This method has never been adopted to any extent in the United States, although it has found favor in England. It may be briefly described as follows.

The foundation course is first prepared as in ordinary macadam work, but its surface should be clean and free from fine material. Upon the foundation is then placed a layer of the prepared matrix, to the depth of approximately 1 inch, called the sub-binder. This matrix should be spread lightly and evenly and on no account should be consolidated before the wearing course of stone is applied. The wearing course should consist of stone crushed and screened to the uniform size of two to two and one-fourth inches, placed on top of the matrix to a depth of what the inventors call a two stone coat. The stone should be spread from the sub-binder already laid, and should be handled with stone forks so as to leave the smaller fragments and the dust behind as waste. This course is brought to within 6 inches of the forward end of the subbinder, after which another strip of sub-binder can be laid for about 3 feet ahead and followed with the application of coarse

stone, always leaving at least 6 inches length of the binder projecting, and so on. By this means the working force will be enabled to lay both sub-binder and wearing course without trampling on either. As soon as a section 25 to 30 feet in length has been laid in this manner, it is rolled with a fairly light roller, the object being to press the coarse aggregate into the sub-binder and at the same time entice the binder upward into the voids of the aggregate. The roller should be run at low speed and when the sub-binder appears in places at the top, a light application of fresh matrix is salted over the road in sufficient quantity to fill the surface voids and the rolling continued until the road is solid. A seal coat of hot bitumen is then applied and the surface sanded and rolled.

This method may be considered as a combination of the penetration and the mixing methods and is open to the criticism urged against the former. That is, uniformity in the resulting road is never assured. The method aims to produce a wearing course of fairly large sized stones which are bound together and the voids between which are filled with the bituminous matrix. This condition of affairs is never a certainty as it is a difficult matter to work the sub-binder uniformly throughout the course. A fluid refined tar has been almost exclusively used in such work. About 15 gallons of the tar are mixed with one cubic yard of sand or stone chips to form the matrix. Repairs may be made by cutting out worn places to expose clean surfaces and refilling with fresh material in the same manner as though constructing a new road.

Characteristics of Bituminous Macadam. — The appearance of a well-constructed bituminous macadam after being subjected to traffic for a short time should be that of a mosaic surface in which the larger stones predominate. These large stones take up most of the wear and are held in place by the filling of smaller bitumen covered fragments. The road should be firm, resilient and waterproof. The surface should be even but not so smooth as to be slippery, the coarse grained aggregate offering sufficient toe hold for horses even on comparatively steep grades. The surface is dustless in the same sense that an ordinary asphalt street is dustless. Resistance to traction is less than that of an ordinary macadam unless too much bitumen has been applied. While the binder is not supposed to bear any great amount of external wear it exerts a cushioning effect between the individual stones and reduces internal wear by preventing them from grinding one against the other, under the action of traffic. A few days after being laid all odor of an objectionable nature will have disappeared. Tar in particular, however, retains its hygienic and germicidal



FIG. 35. Method of Patching Bituminous Macadam Surfaces.

properties for some time after application. To determine this point an investigation of the relative number of living germs existing in the atmosphere just above a tarred and an untarred road in the same neighborhood was made in France by Christiani and Michelis, who found less than one-half the number in the former case as the latter, both in damp and dry weather. The chief recommendation of the bituminous macadam, however, is its ability to successfully withstand the modern combined automobile and horse drawn traffic.

Probably the most critical period in the life of a bituminous macadam is the first two or three months after it is laid, and during this period it should be carefully watched and any needed repairs attended to at once. The green road may rut slightly under heavy traffic and even when constructed with the greatest care is apt to develop weak places. Unless these are repaired at once they serve as starting points for rapid disintegration. After the road has once seasoned, however, there is much less cause for apprehension, and from then on the cost of maintenance should be much less than for ordinary macadam.

Repairs should be made by cutting out all defective places for a depth of about two inches as shown in Fig. 35. The holes should have sharp vertical sides which are smeared with hot bitumen. The old stone is replaced with fresh bituminous concrete and the patch tamped even with the surrounding road surface.

Character of Aggregate for Bituminous Macadam. — Bituminous macadam has the advantage over ordinary macadam of being less dependent upon the quality of the stone for good results, and many rocks which are unsatisfactory for the latter may be used to advantage in this class of work. Thus in straight macadam much is dependent upon the cementing value of the rock, while in bituminous macadam this factor need not be considered, as the bitumen is the only binder to be taken into account. In like manner rocks which are deficient in hardness, toughness and resistance to wear, from the standpoint of regular construction, will often prove serviceable in a bituminous macadam, as they are protected to a considerable extent from the wear and tear of traffic by the cushioning effect of the bitumen. By this is not meant that any material no matter how soft and crumbly may be successfully used, but only that much lower standards may be set. Hard, tough rock will of course produce more lasting results if the proper binder is employed, but the softer varieties, such as limestone and dolomite, may often prove satisfactory, particularly if it is necessary to use a rather fluid bitumen. This is due to the fact that the greater quantity of the fine products of wear are mixed with the binder under traffic and increase its consistency to a considerable extent. In England blast furnace slag has been successfully employed in the construction of tarred-slag macadam and some few experiments have been conducted along this line in the United States.

Blast furnace slag is extremely variable in its physical and somewhat in its chemical properties even when taken from the same furnace, and in order to obtain good results it is necessary to exercise some care in selection. Thus according to its composition and manner in which it is cooled, it may exist as a dense artificial rock, as a vitreous, glassy mass, or it may be soft, crumbly and honeycombed. Any road surface composed of such a heterogenous mixture will wear unevenly and it is therefore advisable to select only the first type of material for bituminous slag surfaces. Such slag is easily distinguishable by sight from the other varieties and the additional expense of selecting and sorting this material before it goes to the crusher should be fully justified by the better and more lasting character of the road surface of which it is composed. It would seem probable that the softer and more crumbly variety could be utilized to advantage if crushed to the size of screenings to serve as a filler for the coarser and harder fragments. At the present time, too little work has been done in this country to warrant any final judgment as to the best practice in constructing bituminous slag macadam. It would seem, however, that this type of road should receive considerable attention by American road engineers, as vast mountains of slag are produced in this country which at the present time is practically waste material and, therefore, much cheaper than rock in localities near which it is produced.

Patent and Proprietary Bituminized Aggregates. — In England a number of patent and proprietary mixtures of bitumen with various mineral aggregates are to be found. These mixtures are prepared at a central plant from which they are shipped

to the consumer ready for application to the road. They are laid cold and for this reason a bitumen of softer consistency than is desirable for construction work is used in order that the concrete may be handled and laid without difficulty. "Tarmac" and "Quarrite" are perhaps the most widely known preparations of this nature, and have been used with some degree of success. A brief description of the former will give some idea of the general character of these preparations.

Tarmac consists of crushed blast furnace slag coated while hot with a tar preparation composed of tar, pitch, Portland cement and resin in substantially the following porportions:

| Tar92.56% by weight |
|-----------------------|
| Pitch 5.79% by weight |
| Portland cement |
| Resin 1.24% by weight |

In the preparation of this compound the tar is first heated to 100° C. and the other ingredients added and thoroughly mixed. It is then employed as a coating for dry or warm slag, the concrete being prepared in a steam jacketed mixer. The slag is crushed and screened into three sizes and in some cases is taken directly from the blast furnace while it is still hot. The prepared concrete may be stored for some time before using.

The Tarmac road is built in a manner quite similar to an ordinary macadam except that of course no water is used. Three courses of tarred slag are laid and rolled separately. For the bottom course two and one-half inch gauge is employed, for the wearing surface one inch gauge, and on top of this a course of tarred slag sand or screenings. All of the road metal is, therefore, covered with tar. While this is by no means an objectionable feature, it raises the cost to over double that of an ordinary macadam even in places where the material is prepared and used at the same place. It is probable that nearly if not equally as satisfactory results could be obtained by using only a two inch wearing surface of the tarred slag laid upon an ordinary broken stone foundation.

Walker Smith, in his treatise on tar macadam, expresses his opinion of Tarmac as follows, and this may perhaps be taken as representing the English idea of this material.

"Much has been heard of 'Tarmac' and much has been claimed for it, and the author must admit that when he first tried 'Tarmac' as an experiment, before visiting their works, he was a little prejudiced against it, principally on account of the variability of the slag and to some extent on account of the specification of the matrix appearing to lend itself to much variation in quality; but he has found that it wears evenly and is very much more economical than granite macadam, but that it wears more rapidly than granite tar macadam."

In the United States ready prepared bituminous concretes for use in road work have been but recently exploited. Of these two may be mentioned, "Warrenite" and "Amiesite." The former is a modification of the well known "Bitulithic" concrete, the latter is a patented preparation made by coating cold crushed stone with a fluid asphaltic cement, and lime. esite" is prepared at the quarry, and to facilitate handling and prevent solidification of the concrete before being laid, about one-half peck of dampened sand is mixed with each cubic yard of the bitumen covered stone. This material is said to sell for about \$3.50 per cubic yard at the quarry. It is laid and rolled cold to any desired depth, either upon an old roadbed which has been reshaped or upon a new foundation of broken stone. At the present time none of the roads constructed of "Amiesite" have been down for a sufficiently long time to warrant an opinion of its serviceability. The author has had occasion to examine a very small section cut from such a roadway, mainly for the purpose of ascertaining the percentage of bitumen and lime. While this examination is very incomplete, owing to the smallness of the sample, it is given below for the purpose of showing the general characteristics of this material.

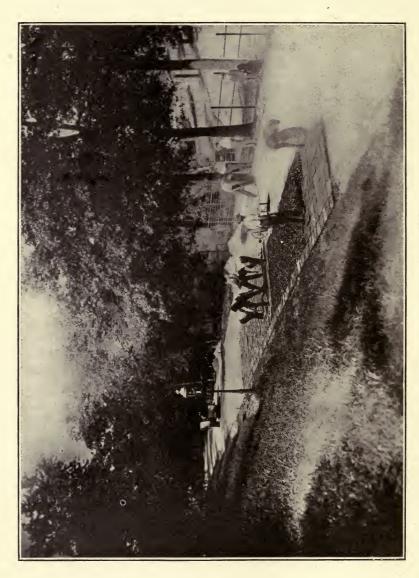
AMIESITE.

| Character. | Bitumen Coated Mineral Aggregate. |
|--|-----------------------------------|
| Soluble in CS ₂ (total bitumen) Specific gravity extracted bitumen 25°/25° C. Per cent bitumen insoluble in 86° naphtha. Per cent ash in extracted bitumen. Lime CaO (basis of mineral matter). Lime CaO (basis of bitumen). | 1.004 22.46 2.88 |

Remarks. — This material would seem to be a mineral aggregate coated with a soft asphaltic cement and lime. The ash obtained from this cement indicates the presence of a native asphalt which has been fluxed with a considerable quantity of a heavy residual oil.

Before leaving the subject of ready prepared bituminized aggregates, mention may be made of a process invented by J. C. Travilla. In brief this process consists in manufacturing lightly compacted slabs of a mixture of bitumen, sand, and stone particles and dust in such proportion that the slab will maintain its shape while being handled and transported, but will be sufficiently soft or plastic to permit it to be squeezed into the voids of a newly laid macadam wearing course. This layer of stone, ranging in size from one-half to two and one-half inches. is laid upon any suitable foundation and is lightly rolled. Over this is spread a thin coating of sand or fine stone screenings in sufficient quantity to partially fill the voids. A coat of bituminous cement is applied over the surface thus formed and the slabs then laid close together, as shown in Fig. 36, and given a preliminary rolling sufficient to squeeze the under portion into the surface below. A coating of bituminous cement is then applied and covered with a thin coat of sand or screenings, after which the road is rolled until smooth and firm. Under this final rolling it is claimed that the slabs are welded together to form a continuous surface. This type of road is in effect much like that of the rock asphalt macadam described on page 225.

Summary and Conclusions. — In this chapter the author has described the application of various kinds of tar to macadam road



surfaces and the construction of bituminous macadam roads in general. The character and use of representative types of patented bituminous concretes have also been discussed. It is probable that the use of the latter will always be restricted to within a few hundred miles of the neighborhood in which they are produced, owing to heavy freight rates on their 90 or more per cent of mineral matter, which makes it impossible for them to successfully compete at a distance with the concentrated bituminous binders and local road stone. There is no reason, however, why the average road engineer should not prepare his own bituminous concrete and in many cases any sort of binder which he desires to use, by means of mixing machines especially adapted for the purposes mentioned, some of which have been described above.

While the mixing method is undoubtedly superior to the penetration method of construction, the latter may often be employed to advantage for roads not subjected to excessively heavy traffic. (For very heavy highway traffic the mixing method should be followed, and as has been mentioned earlier in this book, it is probable that the road of the future will consist of a mixed bituminous concrete wearing surface placed upon a cement concrete foundation.) Roads requiring this type of foundation will also require a very dense and strongly bound wearing surface. Considerable attention will have to be given to the grading of the aggregate and only the most powerful forms of bituminous road binders will be used. At the present time there is no need for this form of construction except in very thickly settled districts surrounding some of our large cities, and the author believes that by the exercise of a little judgment in selection the road engineer may obtain very satisfactory results by following the methods described in this chapter.

CHAPTER XIII.

THE EXAMINATION OF BITUMINOUS ROAD MATERIALS AND INTERPRETATION OF RESULTS.

It is to be regretted that at the present time great lack of uniformity exists in the methods of examining bituminous road materials, as adopted by various chemists. The subject being closely allied to the examination of asphalts and asphaltic cements employed in the paving industry, a very natural tendency has been exhibited to make use of the methods already established for such products. The same criticism, however, applies to the examination of these materials, for in spite of numerous attempts to standardize methods, but comparatively few tests are to-day made in exactly the same manner by all laboratories devoted to the examination of paving materials. For a number of years a special committee of the American Society for Testing Materials, composed of some of the most prominent workers in this field, has been engaged in the problem of standardizing methods, with but poor success. During the past year this committee devoted some time to the consideration of standard tests for bituminous road materials, and at the twelfth annual meeting of the Society, during the summer of 1909, proposed certain tentative tests for these materials, which were not, however, for the time being to be adopted as standard. About the same time, at a meeting of the board of directors of the American Society of Civil Engineers, a special committee of engineers was appointed "To Report on Bituminous Materials for Use in Road Construction, and on Standards for their Test and Use." A list of analyses and tests was formulated by the committee and sent to those interested, requesting them to make such suggestions as seemed advisable and to submit them to the committee, which would then make whatever changes

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it deemed necessary before advocating the analyses and tests as standard.

Both the proposed tests of the American Society for Testing Materials and the revised list of Standard Tests of the American Society of Civil Engineers are given in Chapter XIV for the sake of those who may desire to refer to or use them. It is not the author's purpose here to consider the relative merits and objectionable features of each, but to describe and discuss in some detail tests which from his experience he deems most useful as applied to bituminous road materials. majority of these tests are at present employed in the laboratory of the United States Office of Public Roads, and have been selected as most applicable to the great variety of materials from all parts of the United States which are there examined. It is realized that in view of the comparative newness of the subject no one set of tests can at present be selected which is above criticism, and it is most certain that methods will have to be changed or modified from time to time to meet new conditions as they arise. All tests are not equally applicable to all classes of bituminous compounds, and this is particularly true of tars as compared with oils and asphalts, as will appear

Value of Examination. — Although in the past the examination of bituminous road materials has been sadly neglected, it is now generally admitted that such examinations are very necessary for the intelligent selection and use of these materials. Realization that many experiments have proved unsuccessful because the experimenter had no knowledge of the physical and chemical characteristics of the binder which he used has awakened considerable interest in the testing of bituminous road materials. The old idea that an oil is simply an oil, and if it has produced good results in one locality should produce equally good results in another, has given place to the knowledge that great variations exist in the road building properties of different oils, and that not only will results depend upon the peculiar characteristics of a given material,

but that the method of application and local conditions to which it is subjected are most important factors to be considered. The same is, of course, true of tars and any other class of bituminous binders.

When making an examination a number of factors should be considered, which may often modify the method to some extent. Those of most importance are as follows:

- (1) Purpose for which the material is to be used, *i.e.*, as a dust preventive only, as a semipermanent binder and dust preventive for surface treatment, or as a permanent binder in construction work.
- (2) Character of the road to be treated, including the type of road (earth, gravel, or broken stone) and the physical characteristics of the road material.
- (3) Desired method of application, *i.e.*, whether the material is to be applied cold or hot and by means of a sprinkler, with or without pressure, by pouring from buckets, or as a prepared mixture with the road material. In the latter case it is also desirable to know whether or not the road material itself is to be heated.
 - (4) Quantity and character of traffic.
 - (5) Climatic conditions.

When these facts are known, the examination becomes of more value than simply a means of identification. In any event, however, it serves the latter purpose, and even if an experimenter cannot interpret the results of an examination, he can use them as a guide in duplicating his work under a given set of conditions. Thus if in his work he has found that good results have been obtained from the use of a bitumen having a certain specific gravity, a certain penetration, a certain melting point, certain chemical characteristics, etc., he can be reasonably sure of duplicating these results with another lot of material showing the same characteristics.

Any one characteristic will not, of course, indicate the suitability of a bituminous binder for road purposes, and it is only by considering its collective characteristics that a satisfactory

idea of its value for this purpose can be ascertained. This is particularly noticeable when comparing oils and tars. Thus for construction work an oil product having a specific gravity of 1.08 might be entirely satisfactory, while a tar having the same specific gravity could never be suitable for such work.

Because of the very great difference between oils and tars, somewhat different methods of examination are followed. A summary of the most important tests for each are given at the conclusion of this chapter.

General Characteristics. — When making an examination of any kind of bituminous binder it is well to note its general characteristics, such as,—

- (1) Color by reflected and transmitted light.
- (2) Odor.
- (3) Feel (i.e., whether sticky or greasy).
- (4) Whether smooth or granular.
- (5) Physical state at normal temperature (fluid, semisolid, or solid).

While it is difficult to describe the differences in such characteristics of various types of bituminous materials, it is often possible for one who has acquired some experience in handling and testing them to obtain by this means a fair idea of the kind of bitumen which is to be further examined. Crude oils are usually lighter in color and have a different odor from residual oils, besides being more fluid. Tars are darker in color than the oils and have a characteristic odor which is unmistakable and readily distinguishes them from the former. In mixtures of oil and tar it is often possible to distinguish the odor of each, especially if the product is warmed. Crude tars have a strong gassy odor, which is not so noticeable in refined products. Tars are as a rule more sticky than oils, and the asphaltic oils more sticky than those of a paraffin nature when of approximately the same consistency. Tar products that are lumpy or granular contain an excess of free carbon, and this property in oils is indicative of a considerable amount of paraffin scale. Many other differences might be cited, but as they are all only relative

they serve as an indication only, and not as proof of the kind of material under examination.

Specific Gravity. — (Method.) This determination should be made upon all types of bituminous road materials. The temperature at which the specific gravity is taken should always be stated, in making a report. For most purposes it will be found convenient to make the determination at 25° C. and to express the results as compared with water at the same temperature. This is indicated in a report by the sign 25°/25° C. Some analysts prefer to report the specific gravity in degrees Baumé. The author prefers the direct system, and all specific gravities given in this book are based upon water taken as 1.000. Baumé tables of specific gravity are, however, given in the appendix for the use of those who wish to transpose from one scale to the other.

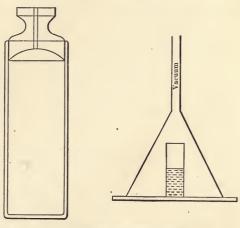
- (a. Hydrometer.) The most convenient method of determining the specific gravity of very fluid bitumens is by means of a thin spindle hydrometer. These hydrometers, graduated in direct specific gravity readings, may be obtained from any dealer in chemical apparatus at small cost, either singly or in sets. One ranging from 1.000 to 1.200 is most suitable for tars, while a set ranging from 0.7000 to 1.000 will be found useful for oils. When the bitumen is too viscous to allow the hydrometer, to settle properly a pycnometer may be employed. One suitable for general use is described below. In some instances very viscous materials are heated up to a point of sufficient fluidity and their specific gravity then taken with a hydrometer, the temperature at which the determination is made being noted. This practice is largely followed by oil chemists, who by means of tables calculate the specific gravity at any desired temperature. The method is not accurate for the determination of all types of bitumen, owing to variations in their coefficients of expansion.
- (b. Pycnometer.) The inconvenience and difficulty of employing the ordinary narrow-neck pycnometer when determining the specific gravity of dense residual oils and soft tar pitches has led the author to devise a modified form suitable for use in this

connection. Except in cases where extreme accuracy is desired, this pycnometer is also suited for determinations of non-volatile oils, especially those of too high viscosity for use with the Westphal balance or hydrometer.

The pycnometer, as shown in Fig. 37, consists of a fairly heavy, straight-walled glass tube, 70 mm. long and 22 mm. diameter, ground to receive a solid glass stopper with a 1.6 mm. bore in place of the usual capillary opening. The lower part of this

stopper is made concave in order to allow all air bubbles to escape through the bore. The depth of the cup-shaped depression is 4.8 mm. at the center. The stoppered tube has a capacity of about 24 cc. and when empty weighs about 28 gms. Its principal advantages are, that (1) any desired be poured in without

touching the sides above



amount of bitumen may Fig. 37. Pycnometer for Determining the Specific Gravity of Bituminous Road Materials.

the level desired; (2) it is easily cleaned; (3) on account of the 16 inch bore the stopper can be more easily inserted when the tube is filled with a very viscous oil than if it contained a capillary opening.

When working with semisolid bitumens which are too soft to break and handle in fragments, the following method of determining their specific gravity has been employed by the author with good results. The clean, dry pycnometer is first weighed empty and this weight called "a." It is then filled with freshly distilled water at 25° C. in the usual manner, the weight again taken and called "b." The bitumen should be brought to a fluid condition by the gentle application of heat, care being taken

that no loss by evaporation occurs. When sufficiently fluid enough is poured into the pycnometer, which may also be warmed, to about half fill it, without allowing the material to touch the sides of the tube above the desired level. If the presence of air bubbles is suspected, the tube may then be placed for a few minutes in a vacuum chamber made by inverting a large glass funnel on a ground-glass plate, as shown in the figure, the edge of the funnel being smeared with desiccator grease. After all air bubbles have thus been removed, the tube and contents are cooled to 25° C. in any suitable manner and weighed with the stopper. This weight is called "c." Distilled water at 25° C. is then poured in until the pycnometer is full, the stopper inserted and the whole weighed. This weight is called "d." From the weights obtained, the specific gravity of the bitumen may be readily calculated from the following formula:

Specific gravity
$$25^{\circ}/25^{\circ}$$
 C = $\frac{c-a}{(b-a)-(d-c)}$.

Both "a" and "b" are constants and need not be determined but once. It is therefore necessary to make only two weighings for all determinations after the first. Results obtained according to the above method are accurate to within two units in the third decimal place as compared with the open-tube method commonly employed, which is accurate to the second decimal place only.

The specific gravity of fluid bitumens may be determined in the ordinary manner with this pycnometer by completely filling it with the material and dividing the weight of the bitumen thus obtained by that of the same volume of water.

The pycnometer may be readily cleaned by placing it in a hotair bath until the bitumen is sufficiently fluid to pour. As much is drained out as possible and the interior swabbed with a piece of cotton waste. It is then rinsed clean with a little carbon bisulphide, and after drying is again ready for use.

(Sommer's method.) A method of determining the specific gravity of asphalts and semisolid substances which deserves

notice has recently been devised by Sommer* who describes the method as follows:

"The main feature of the method is to let the asphalt chill in a small cylindrical vessel which is divided into two parts, the lower holding exactly 10 cc., and the upper being removable from the cup by the connecting thread." (See Fig. 38.) "The principle of the instrument is to have the shrinkage take place in

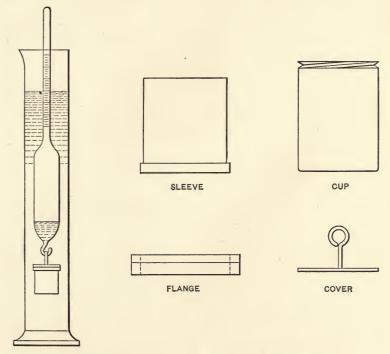


Fig. 38. Sommer's Specific Gravity Apparatus.

the upper, removable sleeve, so that after the removal of the same the lower cup contains a certain fixed volume.

"The entire vessel is filled with melted asphalt and heated for a little while at a temperature slightly above the melting point, in order to thoroughly remove air bubbles or traces of water. After the surface is clear, the vessel is allowed to cool,

^{* &}quot; Proc. Am. Soc. for Test. Mat.," Vol. IX, 1909.

at first in air (to avoid sudden contraction and hence separation of the asphalt from the sides of the tube), and then in water of the desired temperature, which will usually be 60° F. The sample should be left in the water a sufficient time to thoroughly adopt its temperature, and a half hour will not be too long for this purpose. Then it is removed from the water, wiped dry, and the upper extension part or "sleeve" is removed. If the asphalt is so hard that it renders the unscrewing difficult, the upper part should be warmed with a Bunsen burner. The sleeve is then pulled off and the asphalt which extends above the level of the cup is cut off with a broad knife.

"The cup will then contain exactly 10 cc. of asphalt at 60° F. This quantity can be directly weighed on an analytical balance, and the specific gravity ascertained by dividing the number of grams of asphalt by ten. The following method, however, simplifies the procedure:

"After the cup is filled flush, a cover is slid on it from the side, and fastened to it by a flange." . . . "The cup and its contents are then suspended from a special hydrometer and the whole instrument is placed in a jar containing water at 60° F." . . . "If any air bubbles form on the instrument, it should be twisted once or twice quickly and they will escape. The specific gravity can then be read directly on the stem of the hydrometer without correction."

The inventor claims that this method is accurate to the third decimal place and that it is reliable for oils and other semiliquids.

(Interpretation of results.) The specific gravity determination as noted in the above methods is made upon both oils and tars. It is of value mainly as a means of identification, but when considered in connection with other tests is often of service in determining the suitability of the material for road purposes. As applied to oil and oil products, the specific gravity is a rough indication of the amount of heavy hydrocarbons which give body to the material. Crude petroleums vary in specific gravity from 0.73 to 0.98 and slightly higher, paraffin oils as a rule having

the lowest specific gravity and asphalt oils the highest. The former have practically no value for road work, while the latter constitute the most desirable type. Oils containing a semiasphaltic base hold an intermediate position and will usually run higher in specific gravity than the paraffin oils and lower than the truly asphaltic oils. Solid native bitumens free from mineral matter usually have a specific gravity of not over 1.04. If the specific gravity of an oil product or asphalt runs higher than this, the presence of mineral matter is indicated and in native asphalts the increase is almost directly proportional to the amount of mineral matter present, except when the material is very hard and brittle. Thus, a specific gravity of 1.40 indicates the presence of approximately 38 per cent mineral matter, while 1.30 indicates from 20 to 25 per cent mineral matter. This is, of course, only approximately true, as the specific gravity of the asphalt is not only dependent upon the character and consistency of the bitumen itself, but also upon the specific gravity of the mineral matter which it holds. Any oil having a specific gravity of over 0.93 or 0.94 should be heated before application and no natural or residual oil having a specific gravity of less than 0.95 should be employed as a permanent binder. For construction work those lying between 0.98 and 1.00 are to be preferred. If a native asphalt containing mineral matter has been fluxed to suitable consistency for such work, the specific gravity may, of course, run considerably higher.

Crude coal tars vary in specific gravity from 1.10 to 1.25 and sometimes higher, while crude water gas tars lie between 1.00 and 1.10. In coal tars, the specific gravity is largely dependent upon the percentage of free carbon or soot which they contain, those of low specific gravity holding but little and those of high specific gravity holding a large amount of free carbon. Thus a crude tar having a specific gravity of less than 1.15 will usually show less than 12 per cent free carbon, while those running as high as 1.22 will have 30 per cent and over. As free carbon is detrimental to road work, tars of low specific

gravity are as a rule to be preferred. Gas house tars in general are heavier than coke oven tars, produced at low temperature, as they carry a greater percentage of free carbon.

In working upon dehydrated coal tars Kohler* found the following relations to exist between their specific gravity and free carbon contents:

DEHYDRATED COAL TARS.

| Origin of Tar. | of Tar. Specific Gravity. | Urigin of lar | |
|---|--|--|--|
| Heidelberg Darmstadt Baden-Baden Bockenheim Frankfort Bamberg Neustadt Caunstadt Rottweil Karlsruhe Ulm Heilbronn Oos | 1.220 1.215 1.195 1.190 1.180 1.175 1.172 1.164 1.161 1.155 1.150 1.150 | 23.75 20.93 19.92 18.24 15.70 15.15 15.07 14.05 14.00 13.50 12.44 12.42 | |

Determinations of the relation between these properties in refined tars of approximately the same consistency, made in the laboratory of the Office of Public Roads, gave the following results:

REFINED TARS.

| Specific Gravity. | Free Carbon |
|---|--|
| 25°/25° C. | Per cent |
| .216. .230. .239. .245. .256. .262. .273. | 18.63 20.19 21.60 22.50 26.92 28.76 |

^{*} Zsch. f. angew. ch., 1888, p. 677.

In refined tars specific gravity naturally increases with consistency, both because the lighter hydrocarbons and water have been removed and because the relative proportion of free carbon has been increased in the residue. In such products for a given consistency a low specific gravity is to be preferred to a high one. This is not true, however, when considering refined products of different consistencies, as in such cases while the percentage of free carbon might be the same, the most desirable product might show the highest specific gravity for the reasons mentioned above.

As a rule, crude tars having a specific gravity higher than 1.18 cannot be distilled to produce satisfactory road binders, unless previously mixed with a much lighter tar, preferably a water gas tar. No refined tars running lower than 1.16 should be used in construction work, and the same may be said of those running higher than 1.24. The lower limit is set from the standpoint of consistency, while the higher is based upon the

free carbon contents. Any tar having a specific gravity greater than 1.15 should be heated before being applied. Those running under 1.15, which do not have to be heated before application, can be considered as dust layers and temporary binders only.

Flash and Burning Points. — (Method.) A determination of the flash point and burning point of road oils can for ordinary purposes be made according to the open cup method. For this determination the author employs a form of apparatus shown in Fig. 39, known as the Cleveland Oil Tester. This

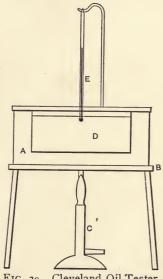


Fig. 39. Cleveland Oil Tester.

oil tester consists of a brass water or oil bath A resting upon the stand B and heated by means of the Bunsen burner C.

The oil to be tested is placed in the brass cup D and the thermometer E adjusted so that its bulb is completely covered with the oil. For very low flashing oils the bath is filled with water or a non-volatile oil, but for high flashing products this space is left empty. Heat is applied so that the temperature of the oil in the cup is raised at the rate of about 5° C. per minute and from time to time a small flame, about the size of a pea, from a capillary glass or metal tube is passed over the oil about half an inch from the surface. The temperature at which the evolved vapors flash is noted and also the temperature at which the oil ignites and burns. The flame should not be blown out at the conclusion of this test for danger of splashing the hot oil. A cover or extinguisher should be employed for this purpose by placing it over the ignited oil.

(Interpretation of results.) This determination is of value as a quick means of differentiating between the heavy crude oils and cut-back products, and the fluid residuums. It also indicates the point to which a refined oil has been distilled and whether or not it is advisable to heat the material before application. Crude oils have, of course, a lower flash point than residual oils and among the crude oils themselves those of a paraffin nature usually flash at a lower temperature than the asphaltic. The former may run as low as ordinary temperature, while the latter are sometimes as high as 135° C. Some crude asphaltic oils will, however, show quite as low flash point as the paraffin oils, so that no great dependence can be placed upon this difference in crude petroleums. The flash point of residual road oils commonly exceeds 200° C., while that of cutback products will vary greatly, according to the flash point of the flux and the percentage and character of the heavier residual product. If it is desired to cut a heavy binding base with a more volatile product, a determination of the flash and burning points of the constituents is of little value in calculating those of the mixture. Sherman, Gray, and Hammerschlag* have shown that these properties are not additive and that the

^{*} Jour. of Ind. and Eng. Chem., Vol. I, No. 1, p. 16.

differences between the calculated and actual results increase with the differences in properties of the two products which constitute the mixture. The following results obtained by the author on mixtures of a petroleum distillate and a heavy petroleum residue are given in the following table. In these experiments it will be noted that there is but little difference in the flash points of those mixtures carrying from ten to sixty per cent of the residue.

FLASH AND BURNING POINT DETERMINATIONS.

| Sample No. | Character. | Flash Point, °C. | Burning Point, °C. |
|--|----------------------|---|-----------------------|
| 0 1 2 3 4 5 6 7 8 9 | Petroleum distillate | 100° 143° 144° 144° 146° 148° 159° 178° 210° 260° | 155° |

Viscosity.—(Method.) The viscosity of fluid bituminous road binders may be determined by means of the Engler Viscosimeter at any desired temperature. This apparatus is shown in Fig. 40, and may be described as follows: A is a shallow brass vessel for the reception of the oil which may be closed by the cover A_1 . To the conical bottom of A is fitted the outflow tube a, exactly 20 mm. long, with a diameter on top of 2.9 mm. and on the bottom of 2.8 mm. This tube can be closed by the pointed, hardwood stopper b, and opened by withdrawing the latter. Three pointed projections c are placed at equal distances from the bottom and serve for measuring the charge of oil, 240 cc. The thermometer t serves for reading the temperature of the material to be tested. The vessel A is surrounded by a brass jacket BB, open on top, which serves for the reception of a heavy mineral oil for heating the con-

tents up to any desired temperature. For temperatures lower than 100° C. water may be used instead of the oil. For observing the temperature of the bath a thermometer is fixed in this medium. A tripod D serves as a support for the whole and

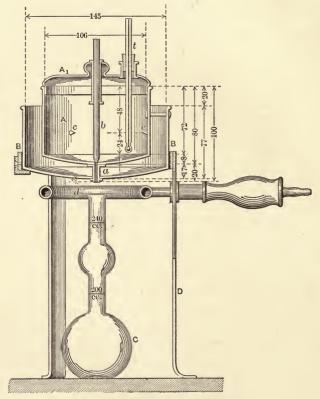


Fig. 40. Engler Viscosimeter.

also carries the ring burner d, by means of which the bitumen is brought to and maintained at the desired temperature. Under the outflow tube stands the measuring flask C. A flask graduated to 50 and 100 cc. is most suitable for road binders.

To work with this apparatus the time must first be determined which is required by water at 25° C. running from it to fill a given volume. The viscosity of the material under ex-

amination is then determined in proportion to that of water at 25° C. Thus if 24 seconds are required for 100 cc. of water to pass through the outlet tube, and 120 seconds for the material examined, the latter would have a specific viscosity of $\frac{120}{24} = 5$.

The test is made as follows: The oil cup and outlet tube are scrupulously cleaned, the stopper inserted in the tube and the cup filled with the road binder, to the mark indicated. The cover is then placed in position and the material brought to and maintained at the desired temperature for at least three minutes. The stopper is then withdrawn and the time required to fill the measuring flask to the desired mark is ascertained by means of a stop watch.

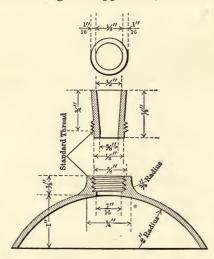
(Value of test.) If for any reason it is desired to apply a road binder at a given temperature, as for instance when it is to be heated by means of steam, a determination of its viscosity at that temperature is often of value. The test also serves as a means of identification. The viscosity of tars containing appreciable quantities of free carbon cannot be accurately determined with this instrument, owing to the clogging effect of the suspended particles. When a viscous material is to be cut with one of lower viscosity in order to bring it to a proper consistency for application, the actual viscosity of the mixture should be ascertained and not calculated from that of the two constituents for the reason that this property is not additive, as has been shown in the same paper referred to under the flash point and burning tests.

Float Test. — (Method.) For materials which are very viscous the float test may be employed as a measure of their consistency. The apparatus used is known as the New York Testing Laboratory Float Apparatus. It is described by Forrest * as follows: "The apparatus, which is made by Howard & Morse, Brooklyn, N. Y., consists of two parts, an aluminum float or saucer, and a conical brass collar. The two parts are shown in the drawing," (see Fig. 41) "and are made

^{*} Eng. Rec., Vol. 59, p. 584.

separately for reasons of economy, so that one or two of the floats will be sufficient for an indefinite number of brass collars.

"In using the apparatus, the brass collar is placed upon a



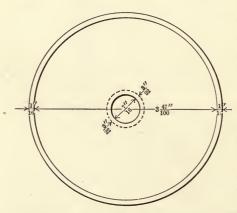


FIG. 41. New York Testing Laboratory
Float Apparatus.

brass plate, the surface of which has been amalgamated, and filled with the bitumen under examination, after it has been softened sufficiently to flow freely by gentle heating. The collar must be level-full, and as soon as the bitumen has cooled sufficiently to handle, it is placed in ice water at 41° F. for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at 90° F. or any other temperature desired.

"As the plug of bitumen in the brass collar becomes warm and fluid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface of the same.

"The time, in seconds, elapsing between placing the apparatus on the water and when it sinks, is determined most con-

veniently by means of a stop watch, and is considered as the consistency of the bitumen under examination."

(Value of test.) The author has employed this test in the examination of a variety of road binders and finds that, while it is an admirable means of identification, it does not always give a true idea of the relative consistency of different classes of bitumens. This is only to be expected when one considers the fact that different products may vary greatly in their specific heats. Moreover, the presence of solid impurities such as mineral matter and free carbon may greatly affect the results. Its main value would seem to lie in its use for control work. The author has had occasion to employ it for this purpose with considerable success in supervising the preparation of road tars. Thus if in refining a given material distillation is continued until the residue shows a definite and predetermined value according to this test, it is possible to turn out a very uniform product in other respects.

If the float test is made upon an oil product it may also be employed to advantage in testing the residue obtained from the volatilization test for the purpose of ascertaining what change in consistency if any has taken place.

Penetration Test. — (Method.) This test, as applied in the examination of asphalts and asphaltic cements for use in the paving industry, is often of value in determining the hardness of semisolid and solid oil and asphalt road binders. A number of machines have been designed for this purpose but the one most generally adopted is known as the Dow Penetration Machine, shown in Fig. 42. The construction of this apparatus and its method of operation as described by Dow are given below:

"The object of the penetration is to ascertain the softness of asphalt, etc., and is accomplished by determining the distance a weighted needle will penetrate into the specimens under examination.

"So that all tests may be comparable, a standard needle should be used, weighted with a constant weight. The tests

should be made on samples at a standard temperature and be made for the same length of time in every case. The standards used in this machine for testing cements to see that

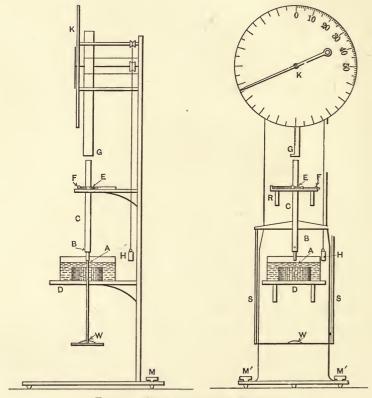


Fig. 42. Dow Penetration Machine.

they are of uniform consistency are a No. 2 needle, weighted with 100 grams, penetrating for five seconds into the sample at a temperature of 77° F. (25° C.).

"The apparatus consists of a No. 2 needle A, inserted in a short brass rod which is held in the aluminum rod C by the binding screw B. The aluminum rod is secured in a framework so weighted and balanced that when it is supported on the point of the needle A the framework and rod will stand in

an upright position, allowing the needle to penetrate perpendicularly without the aid of a support, thus doing away with any friction.

"The frame, aluminum rod, and needle weigh 100 grams with the weight on bottom of frame; without weight, 50 grams. Thus when the point of the needle rests on the surface of the sample of material to be tested as to the penetration, it will penetrate into the sample under a weight of 100 grams or 50 grams as desired.

"The needle and weighted frame are shown in Fig. 42, side and front views of the entire apparatus put together and ready for making a penetration. D is the shelf for the sample, E is the clamp to hold the aluminum rod C until it is desired to make a test, F is a button which when pressed opens clamp E. By turning this button while the clamp is being held open it will lock and keep the clamp from closing until unlocked. The device to measure the distance penetrated by the needle consists of a rack, the foot of which is G. The movement of this rack up or down turns a pinion to which is attached the hand which indicates on dial K the distance moved by the rack. One division of the dial corresponds to a movement of the rack of

 $\frac{1}{100}$ cm. The rack can be raised or lowered by moving counterweight H up or down. L is a tin box containing sample to be tested which is covered with water in the glass cup, thus keeping its temperature constant. M'M' are leveling screws. A clock movement having a ten-inch pendulum is attached to the wall to one side of the machine. Make a mark P on the wall at the extremity of the swing of the pendulum; a double swing of this pendulum, that is, from the time it leaves P until it returns, is one second.

"The only other things necessary to complete the outfit are a large dish pan, a pitcher to hold ice water and a tin for hot water; a coffeepot is a good thing.

"To make penetration tests place the materials contained in circular tins, along with the glass dish, under five or six inches of

water in the dish pan, which should have been previously brought to a temperature of 77° F. by the addition of hot water or cold water.

"While the samples are under the water it should be stirred every few minutes, with the thermometer and the temperature kept constant at 77° F. by the addition of hot or cold water as the case may require. The samples should remain under the water for at least fifteen minutes and in cases where they are very cold or hot, at least one-half hour. The most expeditious way to proceed in testing a sample just taken from a still or tank is to immerse it in ice water as soon as it has hardened sufficiently and keep it there for ten minutes, then in the water at 77° F. and keep it there for fifteen minutes. When the sample has remained in the water for the specified time it is ready to penetrate.

"The aluminum rod C should be pressed up through the clamp E so that it will be at such a height that the glass cup will easily pass under it when placed on shelf D.

"A sample in tin box should now be placed in the glass cup and removed in it covered with as much water as convenient without spilling.

"The glass cup containing sample is placed on shelf D under C. Insert brass rod with needle into C and secure by tightening binding screw B, lower C until the point of the needle very nearly touches surface of sample; then, by grasping the frame with two hands at S and S', cautiously pull down until needle is just in contact with surface of sample.

"This can best be seen by having a light so situated that, looking through the sides of the glass cup, the needle will be reflected in the surface of the sample. After thus setting the needle, raise counterweight H slowly until the foot of the rack G rests on the head of rod C; note reading of dial, place thumb of right hand on R and press button with forefinger, thus opening the clamp.

"Hold open for five seconds and then allow it to close. The difference between the former reading of the dial and the present is the distance penetrated by the needle, or the penetration of the sample. Raise rack, loosen binding screw B, raise rod through clamp, leaving the needle sticking in sample. Remove needle from sample, clean well by passing through a dry cloth, replace needle in C and the machine is ready for another test.

"Do not clean needle on oily cloth, or waste.

"Do not allow rack to descend too rapidly on rod C as it may force C through the clamp, thus spoiling the reading.

"After using the machine, leave it so the top of the rack is just level with its base. You will thus prevent dust from entering and getting into pinion. When not in use keep machine covered with a cloth to protect from dust.

"Examine point of needle from time to time with magnifying glass to see that it is not injured in any way.

"If the needle is found defective, remove by heating the brass rod, when the needle can be withdrawn with pinchers. Break eye from one of the extra needles and press into brass rod previously heated.

"If needle does not stay in well, insert it with a small lump of asphalt.

"If when this framework is supported on the point of the needle it does not balance so that the aluminum rod \mathcal{C} stands perfectly perpendicular, the frame is bent and should be straightened until the rod stands perpendicular. This can easily be done by hand.

"If rack G does not descend readily of its own weight when counter weight H is raised, it is likely that dust has gotten into the pinion. To get at pinion to clean, remove dial K and bearing T, when pinion can be pulled out sufficiently far to clean.

"Never oil rack and pinion, as it prevents a free movement of rack.

"The standards that I have adopted for this test are:

"The distance penetrated by the No. 2 needle into the sample at 32° F. in one minute with 200 grams on frame.

"The penetration at 77° F. as described before, and the pene-

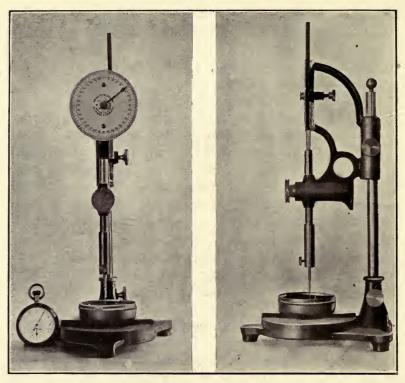


Fig. 43. New York Testing Laboratory Penetrometer. (Portable size.)

tration into the sample of the No. 2 needle in five seconds at 100° F. with 50-gram frame. In some cases I use 100 grams, which is preferable if the depth of the sample will permit. In all cases when you give a penetration of cement state in parentheses how it was made, as, for example, (No. 2 N., 5 sec., 50 grams, 100°) means that the penetration was made with a No. 2 needle penetrating 5 seconds with 50-gram frame at 100° F.

"If a statement is made like this there can never be any doubt about the figures, and they will be understood by all familiar with the machine."

Another type of machine using the same standards and operated in a very similar manner is known as the New York Testing Laboratory Penetrometer. This is made in two sizes, a

laboratory and portable size. The latter is shown in Fig. 43, and is described by Forrest * as follows:

"The diameter of the dial is three inches and the height over all is but eleven inches. The weight upon the needle point is fixed at 100 grams and the time of penetration should be taken by a watch. The hand indicating the degree of penetration is adjustable.

"To adjust and maintain the standard temperature of 77° F. at which the test is made, the instrument and the sample of bitumen, the latter in a tin box one-half inch deep by two and one-half inches diameter, are placed in a tub of water, thus obviating the necessity of adjusting the temperature of the room. A depth of two and one-half inches of water is sufficient."

Whichever instrument is used the results of tests should be reported according to the form suggested by Dow. For the softer bituminous road binders it is often desirable to make the test at 25° C. with a 50 gm. weight, but when possible the results obtained from the 100 gm. weight should also be reported. It is also advisable in many instances to determine the penetration of the residue obtained from the volatilization test as compared with that of the original material in order to detect any change in consistency that has taken place through heating.

(Value of test.) The penetration test, like the float test, is a convenient one to employ for identification and control, and is often indicative of the value of an oil or asphalt product for construction work. While the test for bituminous road materials is made in the same manner as in asphalt paving work, the standards for road purposes are somewhat different. No oil product should be employed in macadam construction with a penetration higher than 25.0 mm. when tested at 25° C. with a No. 2 needle for 5 seconds under a weight of 100 gms., unless it possesses the property of hardening considerably when subjected to the volatilization test. On the other hand, it is rarely

^{*} Proc. Am. Soc. for Test. Mat., 1909, Vol. IX, p. 600.

necessary to require a penetration as high as that for asphaltic cement used in the topping of an asphalt pavement, for the reason that the upper course of a macadam has much greater inherent stability than the sand course of the asphalt pavement. A penetration of from 10.0 to 15.0 mm. is usually considered sufficient for road work. If a material having a much lower penetration is selected, its susceptibility to temperature changes will have to be considered. Blown oils being but little affected by temperature changes may run as low as 4.0 mm: with little danger of becoming too hard in cold weather. They are, however, less ductile than the oil pitches and asphaltic cements of like consistency and somewhat less desirable for road work on this account. The significance of the penetration determination made upon residues obtained from the volatilization test will be discussed under the latter. Penetration determinations are seldom made upon tars, because their surface tension is so high that even approximately correct penetrations cannot be recorded and the presence of free carbon in varying quantities seriously affects the results.

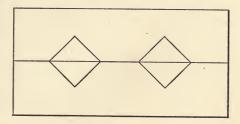
Ductility Test. — A test for ductility has been employed to some extent in the examination of asphaltic cements to be used in the paving industry. It is mentioned here only because a tendency has been exhibited to make use of it in connection with the examination of road binders, and it is difficult to see how it can be of any great value for this purpose. Road binders vary so greatly in consistency that in order to subject them to the test and make it a comparative one, the material should be brought to a definite point of consistency as determined by the penetration method. This can be accomplished by heating it until sufficient volatile matter has been driven off to produce a residue of the desired consistency. This method will, however, often prove to be a long and tedious operation, and in the case of many asphaltic oils results in a chemical alteration due to the application of high temperatures, which produces a residue quite unlike any residue which would be formed under ordinary service conditions. Being an entirely different product, its ductility can in no way be considered a measure of that of the original material.

Such a test may, however, prove of some value if made upon the harder types of bituminous road materials or the residues obtained from the volatilization test described later in this chapter. For a full description of the ductility test reference should be made to a recent paper by Smith.*

Melting Point. — (Method.) Bitumens being mixtures of various organic compounds can have no true melting point, but an arbitrary method for determining the so-called melting point of those materials sufficiently solid to maintain their form for some time under normal conditions, is of value as a means of identification and for control work. The author has tried a

number of methods and has selected the following as being most convenient and accurate for such work.

The material under examination is first melted by the gentle application of heat until sufficiently fluid to pour readily, care being taken that it suffers no appreciable loss by volatilization. It is then poured into a one-half



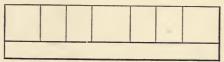


Fig. 44. Brass Cubical Mold. (Double.)

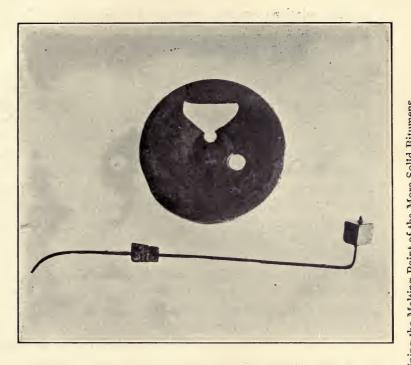
inch brass cubical mold which has been amalgamated with mercury and which is placed on an amalgamated brass plate as shown in Fig. 44. The brass may be amalgamated by washing it first in dilute hydrochloric acid, after which the mercury is rubbed into the surface. By this means the bitumen is to a considerable extent prevented from sticking to the sides of the mold.

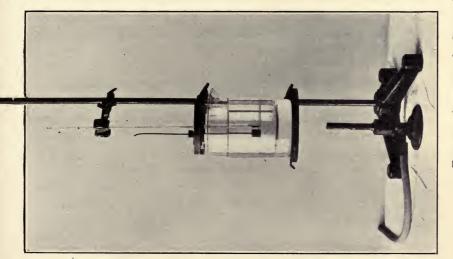
^{* &}quot;A Machine Testing the Ductility of Bituminous Paving Cements." Proc. Am. Soc. for Test. Mat., 1909, Vol. IX, p. 594.

After cooling, the cube is removed from the mold and fastened upon the lower arm of a No. 12 B & S. wire, bent at right angles and suspended beside a thermometer in a covered Jena glass beaker of 400 cc. capacity, which is placed in a water or sulphuric acid bath. The wire should be passed through the center of two opposite faces of the cube, which is suspended one inch above the bottom of the beaker. This piece of apparatus is shown in Fig. 45. The water or acid bath consists of an 800 cc. low form Jena glass beaker suitably mounted for the application of heat from below. The beaker in which the cube is suspended is of the tall form Jena type without lip. The metal cover has two openings. A cork, through which passes the upper arm of the wire, is inserted in one and the thermometer in the other. The bulb of the thermometer should be just level with the cube and at an equal distance from the side of the beaker. In order that a reading of the thermometer may be made if necessary at the point where it passes through the cover, the hole is shaped as shown in the smaller illustration and covered with an ordinary object glass through which the stem of the thermometer may be seen. Readings made through this glass should be calibrated to the angle of observation, which may be made constant by always sighting from the front edge of the opening to any given point on the stem of the thermometer below the cover.

After the test specimen has been placed in the apparatus the liquid in the outer vessel is heated in such a manner that the thermometer registers an increase of 5° C. per minute. The temperature at which the bitumen touches a piece of paper placed in the bottom of the beaker is taken as the melting point. Determinations made in the manner above described should not vary more than two degrees for different tests of the same material. At the beginning of this test the temperature of both bitumen and bath should be approximately 25° C.

(Value of test.) This test can of course be made only on materials intended for road construction. The melting point of a bitumen is directly related to its hardness and brittleness,





but the relations are not the same for all classes. Thus, at normal temperature a blown oil with a melting point of 50° C. is neither hard nor brittle, while a tar pitch is both. As the melting point rises, however, they both become harder and more brittle. For road work, the melting point of a tar pitch should rarely exceed 40° C., while that of a blown product may run as high as 65° C. and over, without fear of the material cracking in cold weather. Oil pitches and the asphaltic cements hold an intermediate position between these two. The climate under which a bitumen is to serve as a road binder could be considered in connection with its melting point, and this is particularly true of tar products. Thus in a cold climate, where the winters are severe, it is preferable to employ a tar pitch having a melting point much lower than 40° C.; in fact, under very severe conditions, one that will melt as low as 20° C.

The desired method of application will also have to be taken into account. If the penetration or grouting method is to be followed, the melting point of a tar product should not exceed 25° C., and in a blown oil probably not over 30° to 35° C., for the reason that if higher than this the material is apt to solidify too quickly upon coming in contact with the cold stone on the road, and will, therefore, not penetrate to any extent. When the mixing method is to be employed using hot stone, the melting point of the bitumen may be as high as climatic conditions will allow. Oil products for application in earth road construction should have a melting point considerably below normal temperature or otherwise it will be extremely difficult to mix them with the cold earth. If the earth can be heated, however, and mixed with the oil before application to the road, a product having a higher melting point is to be preferred.

Volatilization. — (Method.) This test is made in a manner quite similar to the method described by Richardson* for examining refined asphalts. Twenty grams of the material to be tested is placed in a circular tin dish about six cm. in diameter and two cm. deep which has previously been weighed.

^{*} The Modern Asphalt Pavement, loc. cit.

It is then heated in an oven for five hours at a constant temperature of 163° C. and after cooling the percentage loss in weight determined. The oven should be so designed that an even temperature may be maintained, and a thermostat or other mechanical device should be employed to keep the temperature constant. Two thermometers are required, one to show the temperature of the air in the oven and the other immersed in a non-volatile oil to show the temperature of the material tested. The former is of use for determining rapid changes of temperature, so that the supply of heat can be quickly regulated. The temperature of the latter is, however, the one which should govern the final regulation.

It is important that the containing vessels be of uniform dimensions in this test in order to obtain comparative results. When carefully made such determinations are accurate to within about 0.5 of 1%, provided the total percentage of volatile matter is not extremely high.

(Interpretation of results.) That this is not a quantitative determination of any one class of volatile oils which may be present in the original material can be seen in the table following. These results were obtained by determining the loss in weight of two different oils, fresh samples of which were then mixed in the given proportions and the loss determined for the mixtures. It will be noticed that the presence of the less volatile oil retarded the volatilization of the mixture to a considerable extent. It would not therefore seem advisable to designate these volatile materials as a class which may be separated by this means, but to simply report the results as loss upon heating at the given temperature for a given length of time.

VOLATILIZATION TEST OF OIL MIXTURES.

| Oil No. | Character. | Loss. | | |
|------------------|----------------------|--|--|--|
| 1 2 3 3 | Petroleum distillate | 13.13% 12.87% 0.16% 8.45% 8.97% 10.45% | | |

Some analysts make this test upon 50 grams of the material instead of 20 grams. When this is done either a container which will expose a proportionately greater surface should be employed or else the time of the test should be considerably lengthened in order to obtain results at all comparable with the method described above.

While the volatilization test is a purely arbitrary one, when applied to road oils and asphaltic preparations, it will often prove of considerable value. Applied to tars it is of less value because of misleading results produced by the retaining effect, noted on page 262, of the free carbon upon the volatile oils. As applied to oil and asphalt compounds it is believed that the loss in weight thus produced is a fair comparative indication of loss by volatilization suffered by the material in the course of time when applied to the road, also that the character of the residue is similar to that eventually left in the road. A determination of the consistency of this residue should if possible be made, and particular attention paid as to whether it is of a greasy or sticky nature. The volatilization test is not a quantitative determination of any one class of volatile oils present in the original material, but only of its tendency to give up these volatile oils. If the material has a certain consistency which it is desired to maintain after application, it should show a low volatilization and should not be subject to hardening by oxidation or other causes. A determination of penetration of the residue as compared with that of the original material is of value in determining this fact. A material which must be soft and sometimes fluid on account of the desired method of application and character of the road treated should very properly suffer high loss by volatilization in order that it may be capable of attaining proper consistency under service conditions. This is particularly true of oils that are to be applied during the construction of oiled earth roads, in which case a loss of from 20 to 30 per cent is not uncommon. Fluid products that will not volatilize to any extent nor harden under this test are unfit for any sort of construction work and their use for this purpose can only

result in failure. The great bulk of residual oils belongs to this class of materials. If the residue shows a penetration of over 25.0 mm. the material will never prove satisfactory, except in roads subjected to very light traffic. As a rule, it may be said that other things being equal, the suitability of an oil for use in the construction of roads increases as the penetration of its residue decreases. An oil showing a penetration of from 10.0 to 15.0 mm. should suffer but little loss by volatilization, usually less than one per cent, and the penetration of its residue should not be greatly lowered.

Fluid products to be used in the surface treatment of roads need not necessarily show a high loss by volatilization nor a great increase in the consistency of their residues, although the latter is a desirable property. They are mainly of value as dust preventives and binders for the thin coat of fine material upon the road surface and cannot affect the character of the road proper unless applied in large quantities. If their residues are not of a sticky nature, they will, however, produce an undesirable surface condition in wet weather unless applied in very small quantities. In general all residues should be sticky or adhesive, as otherwise they will act more as lubricants than as road binders. A paraffin oil will produce a greasy residue, while an asphaltic oil will produce one that has considerable binding value. It is for this reason that the latter may be successfully employed in road work, while the former are worthless for this purpose.

In certain instances, determinations of the so-called asphalt contents of oils have been made by driving off volatiles until the residue is of a certain consistency. To produce this residue it is often necessary to subject the bitumen to such high temperatures that chemical changes take place which would never occur under service conditions. For this reason the test is not a determination of the actual asphalt contents, but only of the ability of the oil to produce an asphaltic base of given consistency under the action of high temperatures. Such a test is, therefore, misleading and has resulted in much con-

fusion among road engineers as to the relative binding value of oils. This matter has been discussed to some extent by the author elsewhere in this book.

Besides the temperature of 163°C. it may in some instances be advisable to determine the volatilization of a material at 100°C. or even lower in order to ascertain whether or not it is capable of rapidly increasing in consistency under service conditions. In such cases the same general method is followed as described for the higher temperature.

Total Bitumen. — (Method.) For practical purposes, all organic matter soluble in carbon bisulphide (or carbon disulphide, as it is often called) is considered as bitumen in this determination and the total bitumen found by digesting the material to be examined in this solvent and filtering off the insoluble residue. The method which the author employs is practically identical with the "Rapid Method for the Determination of Material in Bituminous Road Compounds Insoluble in Cold Carbon Disulphide" suggested by the American Society for Testing Materials. From one to ten grams of the water-free material (depending upon the amount of bitumen present) are weighed into a 150 cc. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 cc. of c.p. carbon bisulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside for not less than fifteen hours. At the end of this time the contents of the flask are decanted off upon a weighed Gooch crucible fitted with a long-fiber amphibole asbestos filter. The residue remaining in the flask is then washed with 50 cc. of carbon disulphide, allowed to settle, and decanted as before, the insoluble matter being finally brought upon the filter and washed with 100 cc. carbon disulphide, or until the washings are practically colorless. The filter and contents are then dried at 125° C., cooled and weighed. Should any residue remain in the flask, it is also dried and weighed and this weight added to that of the residue in the crucible. Where great accuracy is desired, the filtrate should be burned off and ignited to an ash and the weight of the ash thus obtained added to that of the insoluble

The weight residue. of the total residue deducted from that of the original material gives the weight of bitumen soluble in cold carbon disulphide. In case of tars and pitches the percentage of insoluble residue, determined as above, minus that of any ash which may be found by ignition, is reported as free In oils it is carbon. reported as organic matter insoluble.

The form of Gooch crucible best adapted for such determinations holds 30 cc., is 4.4 cm. wide at the top, tapering to 3.6 cm. at the bottom, and 2.6 cm. deep. The felt is made by beating up the asbestos in a mortar and suspending the finer particles in water. It is well to have a stock bottle of this mixture always



FIG. 46. Filtering Apparatus for the Determination of Total Bitumen.

on hand. The suspended asbestos is poured into the crucible, which has in the meantime been placed in the vacuum filtering

flask as shown in Fig. 46. As soon as the asbestos has somewhat settled vacuum is applied and the felt deposited on the bottom of the crucible, which is then dried, ignited, cooled in a desiccator and weighed. The prepared felt should be dense enough to just barely transmit light when held so that the bottom of the crucible is between the eye and the source of light. it is denser than this the filter is apt to clog, and if much thinner to let through the finer particles of insoluble material. With a little practice it is possible to prepare a uniform felt without difficulty. In the carbon bisulphide extraction it is seldom necessary to make use of the vacuum during filtration, but it is convenient to filter into the vacuum flask, in which case vacuum may be applied if desired. The carbon bisulphide for this determination should be chemically pure and when shaken with a little clean mercury should show no discoloration of the latter.

As applied to asphalts Richardson* has shown that finely divided inorganic material when present retains a certain amount of bitumen which cannot be removed by carbon disulphide, and this is undoubtedly true of some road binders. Free carbon as found in tar probably exhibits a similar absorbent action. For all practical purposes, however, this defect in the method may be neglected. Various forms of extraction apparatus are sometimes employed for this determination, but the method described has been found most suitable for all types of bituminous road materials.

(Value of test.) Fluid oils are almost completely soluble in carbon disulphide, and also blown oils and oil pitches unless they have been cracked to the point of producing free carbon. The solid native bitumens, with a few exceptions, are not so soluble, as they contain more or less mineral matter, together with organic matter of a non-bituminous nature. Thus, petroleums and petroleum products are almost always soluble to the extent of at least 99.5 per cent, and should contain less than 0.2 per cent mineral matter, while the native asphalts may show

^{*} Proc. Am. Soc. Test. Mat., 1906, Vol. VI., p. 509.

as low as 54 to 56 per cent bitumen. This is characteristic of Trinidad asphalt, an average sample of which will contain approximately 56 per cent soluble in carbon bisulphide, 7 per cent organic matter insoluble and 37 per cent mineral matter. Bermudez asphalt will show in the neighborhood of 95 per cent soluble in carbon bisulphide, and 2.5 per cent each of organic matter insoluble and mineral matter. Gilsonite will more nearly coincide with the oils in this test, being an extremely pure solid native bitumen soluble in carbon bisulphide to the extent of from 99.4 to 99.6 per cent. The solubility of the bitumen itself is entirely independent of its character and consistency, so that the amount and character of insoluble material is of most interest in this test. This material is of no value from the standpoint of road work, but indicates whether an asphalt has been employed in the preparation of the binder, also whether a product has been destructively distilled during its preparation, the determining factor in the former case being the amount of mineral matter present and the amount of organic material in the absence of mineral matter in the latter case. It is of course possible to adulterate a preparation so as to give misleading results, unless the analyst is familiar with the characteristics which the addition of various solid native bitumens will produce in oils of different

Tars, with the exception of those produced in blast furnaces, contain only a small fraction of one per cent mineral matter. Practically all material insoluble in carbon bisulphide is, therefore, organic material, commonly known as free carbon. The relation of free carbon to the density of tars has already been discussed under the specific gravity determination, which, as has been shown, if taken in connection with the consistency of the tar, gives a good indication of the percentage of this constituent.

Any tar or tar product containing less than 4 per cent free carbon may almost, without exception, be considered as originating in the manufacture of carburetted water gas and is the product of the destructive distillation of oil. Water gas tars or oil tars will usually contain less than this amount, even when refined to a specific gravity of 1.17, and crude water gas tar seldom exceeds 2 per cent free carbon. Most crude coke oven tars will carry from 4 to 10 per cent free carbon, unless they have been produced at very high temperatures, while the modern gas house coal tars rarely show less than 15 per cent and sometimes run as high as 30 per cent and over.

The effect of free carbon in tars from the standpoint of road treatment has been fully discussed in Chapter XI.

Free Carbon. — This determination as applied to tars is described under the total bitumen determination. Some analysts use benzol as a solvent in place of carbon bisulphide, and employ an extraction apparatus. As a rule the results obtained with both solvents are sufficiently close to make little practical difference, but it is always well when reporting this constituent to state the solvent used and the method of determination, that is, whether the Gooch crucible or extractor has been employed. In this book free carbon should be understood as material insoluble in carbon disulphide according to the Gooch method.

Bitumen Insoluble in 86° B. Paraffin Naphtha. — (Method.) This determination is made in the same manner as the total bitumen determination except that 86° Baumé naphtha is employed as a solvent in place of carbon disulphide. The test is made only upon oil and asphalt products and the per cent of bitumen insoluble is reported upon the basis of total bitumen taken as 100. The difference between the material insoluble in carbon disulphide and in the naphtha is the bitumen insoluble in the latter. Thus if in a certain instance it is found that the material insoluble in carbon disulphide amounts to 1.0 per cent and that 10.9 per cent is insoluble in naphtha, the per cent of bitumen insoluble would be calculated as follows:

$$\frac{\text{bitumen insoluble in naphtha}}{\text{total bitumem}} = \frac{10.9 - 1}{100 - 1} = \frac{9.9}{99} = 10 \text{ per cent.}$$

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The great objection to this determination is that petroleum naphthas are by no means definite compounds, being composed of a number of hydrocarbons which vary in character and quantity according to the petroleum from which they have been distilled. Their solvent powers also vary greatly. Thus naphthas produced from asphaltic petroleums, consisting mainly of naphthene and polymethylene hydrocarbons, are much more powerful solvents of the heavier asphaltic hydrocarbons than are the paraffin naphthas. The density of the naphtha also affects its solvent power, those of high gravity dissolving the heavier hydrocarbons more readily than those of lower gravity. As the main object of this test is to separate the heavier hydrocarbons of an asphaltic nature from the paraffin hydrocarbons, a paraffin solvent should be employed and for ordinary purposes the author has found a paraffin naphtha of 86° Baumé gravity, boiling between 40° and 50° C., to be readily obtainable and fairly satisfactory. The solvent action of 88° naphtha is a little lower and, therefore, preferable, but it cannot be as readily obtained. The use of a definite paraffin compound such as pentane or hexane has been suggested for this determination, but these products are very expensive and although they would be preferable to naphtha in many respects, until some method is devised by which they may be completely recovered so as to be available for repeated use, they are unlikely to be generally adopted. It is difficult to employ an extractor for this determination, owing to the clogging of the filter, which frequently necessitates the use of a vacuum. When vacuum is employed the loss of the solvent by volatilization is very appreciable.

(Value of the test.) The term asphaltenes is commonly applied to bitumen insoluble in petroleum naphtha, and malthenes to that portion which is soluble. It is of course evident that both of these terms cover a multitude of compounds, but in general it may be said that the asphaltenes tend to give body and consistency as well as adhesive properties to the products in which they are found, so that this determination serves as an

indication of the mechanical stability of the material as well as its binding qualities.

No oils carrying less than 4 per cent naphtha insoluble bitumen will prove of service other than as dust preventives. Crude paraffin oils are almost entirely dissolved by this solvent, while the asphaltic oils contain very appreciable amounts of naphtha insoluble bitumen. Residual oils carry larger quantities than the crude oils from which they are produced, and blown oils, in particular, show very high percentages of insoluble hydrocarbons, sometimes running as high as 25 to 30 per cent. In this type of oil the naphtha insoluble bitumen increases with the amount of blowing to which the oil has been subjected, as shown by the following results taken from a patent by Culmer and Culmer:*

EFFECT OF BLOWING OILS.

| Hours Blowing | Per cent Asphaltenes. |
|---------------|-----------------------|
| 0 | 2.50% |
| 16 | 8.03% |
| 32 | |
| 40 | 25.14% |

The solid native bitumens also run high in this respect, Trinidad and Bermudez asphalt showing 35 to 40 per cent insoluble bitumen, and gilsonite as high as 45 per cent. Asphaltic cements containing appreciable quantities of these solid products will necessarily show relatively high percentages of bitumen insoluble in naphtha. While the binding value of asphaltic oils and cements is undoubtedly dependent upon the presence of the naphtha insoluble hydrocarbons, variations in the character of these hydrocarbons exert a marked influence upon the characteristics of the original material. This matter has at present received but little attention and just what such differences are and what effect they have is a matter for future study. The character of the naphtha soluble bitumen after the solvent has been evaporated is of interest from the standpoint of road treatment, that which is sticky after the solvent has been evaporated indicating better road building qualities in the original material than that which is greasy.

^{*} U. S. Patent No. 635,430.

Determination of Bitumen Insoluble in Carbon Tetrachloride. - This determination is made in exactly the same manner as described for the total bitumen determination, except that carbon tetrachloride is employed as a solvent. As in the case of the naphtha insoluble bitumen, the results are calculated upon the basis of the total bitumen present. Unless an oil has been badly cracked or a solid bitumen such as grahamite added, this determination is not usually necessary, as the difference between it and the total bitumen determination will be negligible. Only when the per cent of hydrocarbons insoluble in 86° naphtha is found to be high should it be employed. The bitumens insoluble in carbon tetrachloride have been termed carbenes, and in some instances have been included in asphalt specifications. But little is known of their effect upon the physical properties of the oils and asphalts in which they are found, but as has been shown by Kirschbaum,* they are "the result of unnecessarily high temperatures and resulting concentration in the production or refinement of large quantities of both natural and oil asphalts." It is therefore a matter of interest to note any considerable amount of these products in oils which are to be used as road binders, for the purpose of determining their effect upon the practical results obtained. Most road oils will be found to be equally soluble in carbon tetrachloride and carbon disulphide. While the solid native bitumens all show a certain percentage of carbenes, grahamite runs particularly high in this class of hydrocarbons. Carbenes may, therefore, be expected to occur in appreciable amounts in road binders pre-

Fixed Carbon. — (Method.) This determination is made in accordance with the method described for coal in the Journal of the American Chemical Society, 1899, Vol. 21, page 1116. One gram of the material free from water is placed in a platinum crucible weighing from 20 to 30 grams and having a tightly fitting cover. It is then heated over the full flame of a Bunsen burner for seven minutes. The crucible should be supported

pared from this material.

^{*} Mun. Engineering, Vol. XXXV, No. 6, p. 349.

on a platinum triangle with the bottom 6 to 8 cms. above the top of the burner. The flame should be fully 20 cms. high when burning free, and the determination should be made in a place free from drafts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon.

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100 per cent, with the volatile hydrocarbons, excluding the inorganic matter.

(Value of test.) The fixed carbon determination shows much the same thing as that for naphtha insoluble bitumen, as it serves as an indication of the mechanical stability of an oil. Paraffin oils show but little fixed carbon, while the asphaltic oils run higher and the asphalts still higher. The terms fixed carbon and free carbon should not be confused, as they have entirely different meanings. Free carbon always exists as such in the material, while fixed carbon is the coke resulting from ignition of the bitumen in the absence of oxygen. Fixed carbon determinations are seldom made upon tars, as the presence of free carbon interferes with this test. Owing to a misconception as to what fixed carbon represents, specifications have sometimes been made limiting the percentage of this substance to a very low figure. Providing that free carbon is absent, comparatively high percentages of fixed carbon are a rather desirable property in oils, for the reason before mentioned, especially if they are to be used in construction work. Native asphalts average from 12 to 14 per cent. No asphaltic cement suitable for construction work according to the mixing method will probably show less than 6 per cent fixed carbon, but too great reliance should not be placed upon this determination, as it is not a very accurate one and is employed more as a means of identification and as a comparative test for the naphtha insoluble material than for any other purpose.

Paraffin Scale.—(Method.) This determination may be made upon oil products according to the method employed by the Standard Oil Company.

"One hundred grams of the oil is distilled rapidly in a 6 ounce retort to dry coke.

"Five grams of the well-mixed distillate is treated in a

2 ounce flask with 25 cc. Squibb's ether; after mixing together thoroughly, 25 cc. Squibb's absolute alcohol is added, and the flask packed closely in a freezing mixture of finely crushed ice and salt for at least thirty minutes. Filter off the precipitate quickly by means of a suction pump, using a No. 575 C. S. & S. 9-cm. hardened filter, cooled by the above freezing mixture in a suitable apparatus.

"Rinse and wash the precipitate with I to I Squibb's alcohol and ether mixture cooled to o° F. until free from oil. Fifty cc. of the washing solution is usually sufficient. When sucked



FIG. 47. Filtering Apparatus for the Determination of Paraffin Scale.

dry, remove the paper, transfer the waxy precipitate to a small glass crystallizing dish. Dry on a steam bath and determine the weight of paraffin scale remaining in the dish.

"Weight of paraffin scale divided by weight of distillate taken, and multiplied by per cent of total distillate obtained from the original sample, equals per cent of paraffin scale."

A convenient form of filtering apparatus is shown in Fig. 47. The suction flask carries a rubber stopper through which passes the stem of a funnel. The stem of this funnel also passes through a stopper in the container which holds the freezing mixture. This container may be made by cutting the bottom from a bottle of suitable dimensions.

(Value of test.) While the general character of an oil as shown by the base obtained from the volatilization test is ordinarily a sufficient indication of its paraffin contents, this determination is sometimes of value. The author believes, however, that in most cases it is unnecessary. In road oils the heavy liquid paraffins, when present in excessive amounts, probably exert a much more undesirable influence upon practical results than the solid paraffins, and for this reason it is believed that in most cases a determination of the latter can be dispensed with. It is possible for manufacturers to distill paraffin oils in such a way as to remove practically all paraffin wax from the residues and such products are no more desirable than if the wax were present.

Distillation Test. — (Method.) This test is made upon tars and tar products as follows: From the specific gravity of the tar, taken at 25° C., the weight of 250 cc. is calculated and this amount poured into a tared glass retort of 750 cc. capacity. A cork stopper carrying a thermometer is then inserted in the tubulature so that the bulb is on a level with the bottom of the juncture of stem and body of the retort, as shown in Fig. 48.

The tar should be heated gradually by means of a Bunsen burner and the first fraction to 110° C. caught in a graduated glass cylinder. A cold wet towel wrapped about the stem of the retort serves to condense the distillate. If the tar is a crude one containing much water, great care must be taken to



Fig. 48. Distillation Test Apparatus.

prevent it from boiling over. After the first fraction is collected, however, distillation proceeds without trouble. At this point the receiver is changed for another graduated glass cylinder and an asbestos paper cover (see Fig. 49) placed over the retort for the purpose of obtaining a uniform temperature. The flame of the burner should be so regulated that not over

two drops of distillate per second are collected. At 170° C. the receiver is again changed and a third fraction to 270° C. collected. Distillation is then stopped, and any material which may have solidified in the stem of the retort is liquified by the application of heat and caught in the last receiver. When the

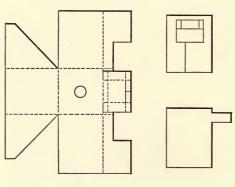


Fig. 49. Asbestos Cover for Retort.

(Fold along dotted lines and fasten together with platinum or copper wire staples.)

maximum temperature is reached for each fraction the flame should be removed from under the retort until the thermometer shows a drop of about 5 degrees. The temperature is then raised very slowly to the maximum again before the graduate is changed for the next fraction. In this manner very uniform results may be obtained.

If water was present in the tar it will be noticed that the first fraction separates into two layers, the lower of ammoniacal liquor or water and the upper of oil. All of the fractions are cooled to 25° C., their volume percentage calculated and that of the pitch residue determined by difference. The per cent of pitch and the various distillates upon a weight basis may also be determined, and note made of the approximate volume of solids which precipitate from the distillates upon cooling to 25° C. Distillations carefully conducted according to the method described give quite comparable results.

The results obtained are reported as follows, to half of I per cent:

% by vol. % by wt. 1. Water or ammoniacal liquor.....

- 2. First light oils to 110° C
- Second light oils 110° C. to 170° C.....
- 4. Heavy or dead oils 170° C. to 270° C
- Pitch residue by difference.....

(Value of test.) The distillation test as applied to tars is a very valuable one, both for the purpose of ascertaining their road building properties and method of preparation if they are refined products. All crude tars contain water, which of course appears in the first fraction to 110° C. In coal tars this water is ammoniacal, while in water gas tars it is not. No tar containing water should be employed as a permanent binder and even in temporary binders its presence is detrimental. Refined tars for use in road construction, if of suitable original consistency for permanent work, should not contain over 7 or 8 per cent by volume of distillate up to 170° C., and this distillate, together with that lying between 170° and 270° C., should when cold show but little precipitated naphthalene. The napthalene contents of the last fraction will often differentiate the plain residual coal tar pitches from cut back products. In the former this fraction will usually run from one quarter to three-quarters solid naphthalene, while in the latter it will run much lower, owing to the fact that these oils have been separated from naphthalene before using them as a flux. Naphthalene is an undesirable constituent of road tars, as it gives the product a false consistency and volatilizes quite readily. It is usually found in coal tars to a greater extent than in water gas tars. In all tars to be used in road construction the total distillate to 270° C. should not exceed 50 per cent by volume of the original material, or otherwise the product will be deficient in true binding base, especially if its free carbon content is high. For surface treatment this distillate may run higher, as the lighter oils are necessary to give the tar a proper degree of fluidity for application, especially if the application is to be made cold. In cold climates a high percentage of heavy oils lying between 170° C. and 270° C. is desirable, as they reduce the brittleness of the material.

Tars which have been simply dehydrated often carry as high as 10 to 18 per cent of light oils between 110° C. and 170° C. if produced by destructive distillation of coal. Dehydrated water gas tars will usually run much higher in this respect. These

oils are of no value for road purposes, except when it is desired to use a product which will harden rapidly after application.

When a mixture of tar and oil products is suspected, the distillation test will often decide the matter very definitely. Petroleum and tar distillates obtained between two given temperatures will vary in specific gravity, the petroleum distillate being lighter than the tar distillate. If distillation is conducted carefully a separation of these two products will often take place in the receiver, forming two distinct layers of oil. This will not happen if either a pure tar or pure petroleum product is distilled. If desired, the separate distillates may be identified by suitable chemical means. Any naphthalene which may pass over and precipitate out of the distillate is almost conclusive evidence of the presence of tar. Both the tar and petroleum distillates have very characteristic odors, which may usually be distinguished even in a mixture of the two.

Examination of Bituminized Aggregates. — When it is desired to analyze a bituminized aggregate enough of the sample to supply about 60 grams of bitumen is selected for examination. Thus if a mixture contains 6 per cent bitumen a 1000 gram sample is selected. The material should be covered and digested for about twelve hours, in a suitable dish, with carbon disulphide. The supernatant liquid is then decanted off, fresh solvent added and the process repeated, after agitation, until practically all of the bitumen has been removed. The decanted solutions are then poured through a large paper filter and the filtrate distilled until the residue is of syrupy consistency. It is then poured into an evaporating dish and heated for some time on a steam bath, after which it is placed in a hot air oven at not over 100° C. until the last traces of carbon disulphide have been removed. The recovered bitumen may then be examined in the usual manner.

The residue remaining on the filter should be dried, ignited and added to the rest of the mineral matter, after which a separation of the aggregate can be made by screening it into various sizes.

Summary and Conclusions. — The foregoing description of tests, for bituminous road materials and the interpretation of results for same, should enable the road engineer not only to make an intelligent examination of materials which he has occasion to use, but also to judge from such examination as to the value of any given material for a given purpose. As was stated early in this chapter, a number of factors should be considered when making an examination, which may modify the method to some extent. When a mixture of tar and oil or asphalt is suspected a somewhat different method may have to be employed than when the product belongs to a single type; some tests, such as determinations of the melting point and penetration of a material, cannot always be made; emulsions may require slightly different treatment from the plain binders: and the analyst must therefore exercise some judgment in regard to an examination. In most cases, however, bituminous road materials may be broadly classed either as oil or tar products. A list of those determinations which the author considers most important for each class is given below

OIL AND ASPHALT PRODUCTS.

- (1) Specific gravity
- (2) Flash point.
- (3) Melting point of solids.
- (4) Penetration of semisolids and solids.
- (5) Volatilization at 163° C. five hours.
 - a. Melting point of residue.
 - b. Penetration of residue.
- (6) Solubility in carbon disulphide.
 - a. Total bitumen.
 - b. Organic matter insoluble.
 - c. Inorganic matter.
- (7) Bitumen insoluble in 86° Naphtha.
- (8) Fixed carbon.

TAR PRODUCTS

- (1) Specific gravity.
- (2) Melting point of solids.
- (3) Free carbon.
- (4) Results of distillation.
 - a. Water.
 - b. First light oils to 110° C.
 - c. Second light oil 110°-170° C.
 - d. Heavy oils 170° -270° C.
 - e. Pitch residue.

In conclusion it may be said that under the interpretation of results and value of test, only the very broadest limitations have been set with regard to the effect of physical and chemical properties upon the suitability of a material for a given purpose. This is due to the necessarily broad discussion of the subject. For individual cases it will often be found necessary to draw these limitations closer if best results are to be obtained in practice.

CHAPTER XIV.

METHODS OF EXAMINATION PROPOSED OR ADOPTED BY AMERICAN SOCIETIES.

American Society for Testing Materials (1909).

REPORT OF COMMITTEE H ON STANDARD TESTS FOR ROAD MATERIALS.

Your committee on Standard Tests for Road Materials has made considerable progress during the past year. After careful consideration, the method for the determination of bitumen in asphalt paving mixtures, refined asphalts and asphalt cements, which was reported and accepted by the society in 1906, has been revised so as to include all bituminous paving and road material. It is believed that this revision can be made without a further investigation by the examination of various samples by members of the committee and other analysts, as was done before the presentation in 1906 of the method referred to above.

The committee, in presenting this method of analysis, wish it understood that they do not recommend it as the best for general use, as it is longer and in several cases gives no better results than other more expeditious methods, but only as a method to be resorted to in case of dispute. A rapid method, which is suggested for general use, is also given.

The committee further recommends the methods for sizing and separating the aggregate in asphalt paving mixtures and determining the consistency of bitumens by penetration, as reported to the society in 1906 and published in the proceedings for that year.

Methods for the determination of the loss on heating of oil and asphaltic compounds, and the determination of residual

coke in bitumens, are herewith submitted to the society for the first time.

All of the tests for bituminous compounds for roads and pavements referred to above follow as an appendix to this report.

Respectfully submitted on behalf of the committee,

LOGAN WALLER PAGE, Chairman.

PRÉVOST HUBBARD, Secretary.

APPENDIX.

Proposed Tests for Bituminous Compounds for Roads and Pavements, Including Method of Sizing and Separating the Aggregate in Asphalt Paving Mixtures.*

METHOD FOR THE DETERMINATION OF BITUMEN IN PAVING COMPOUNDS, INCLUDING THE DETERMINATION OF BITUMEN
IN ASPHALT PAVING MIXTURES, REFINED ASPHALTS,
ASPHALT CEMENTS, BITUMEN-TREATED ROAD
MATERIALS, TARS AND TAR PITCHES,
SOLUBLE IN COLD CARBON DISULPHIDE AND OTHER
SOLVENTS.

Drying the Sample and Preparing it for Analysis.—It was decided, owing to the great variety of conditions met with in bituminous compounds, that it is impossible to specify any one method of drying that would be satisfactory in every case. It is therefore supposed that the material for analysis has been previously dried, either in the laboratory or in the process of refining or manufacture, and that water, if present, exists only as moisture in the hydroscopic form.

The material to be analyzed, if hard and brittle, is ground and spread in a thin layer in a suitable dish (iron or nickel will

^{*} These tests are recommended by Committee H, but the Committee is not yet prepared to advise their adoption as "standards" by the society.

answer every purpose) and kept at a temperature of 125° C. for one hour. In the case of paving mixtures and road materials, where it is not desirable to crush the rock or sand grains, a lump may be placed in the drying oven until it is thoroughly heated through, when it can be crushed down into a thin layer and dried as above. If the material under examination contains any hydrocarbons at all volatile at this temperature, it will of course be necessary to resort to other means of drying.

Analysis of Sample. — After drying, from 2 to 15 grams (depending on the richness in bitumen of the substance) is weighed into a 150-cc. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 cc. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside and not disturbed for forty-eight hours. The solution is then decanted off into a similar flask that has been previously weighed, as much of the solvent being poured off as possible without disturbing the residue. The first flask is again treated with fresh carbon disulphide and shaken as before, when it is put away with the second flask and not disturbed for forty-eight hours.

At the end of this time the contents of the two flasks are carefully decanted off upon a weighed Gooch crucible fitted with an asbestos filter, the contents of the second flask being passed through the filter first. The asbestos filter shall be made of ignited long-fiber amphibole, packed in the bottom of a Gooch crucible to the depth of not over one-eighth inch. After passing the contents of both flasks through the filter, the two residues are shaken with more fresh carbon disulphide and set aside for twenty-four hours without disturbing, or until it is seen that a good subsidation has taken place, when the solvent is again decanted off upon the filter. This washing is continued until the filtrate or washings are practically colorless.

The crucible and both flasks are then dried at 125° C. and weighed. The filtrate containing the bitumen is evaporated, the bituminous residue burned, and the weight of the ash thus

obtained added to that of the residue in the two flasks and the crucible. The sum of these weights deducted from the weight of substance taken gives the weight of bitumen extracted. In the analysis of hard asphalts or tar pitch for their solubility in carbon disulphide and also in the analysis of any of the bitumens for their solubility in naphtha, it is recommended that from 15 to 20 grams of glass beads be introduced into the first flask with the substance. When the flask is shaken, these beads grind up any lump of hard bitumen, and thus greatly facilitate the solution of the soluble constituents. In filtering these solutions through the Gooch crucible, they should be allowed to run through by gravity, as the application of an exhaust appears to cause a clogging of the filtering medium.

This test shall be carried on at a temperature of from 20° to 25° C. When carbon disulphide or carbon tetrachloride are used as solvents, they must be chemically pure. When naphtha is employed, the committee recommends that in all cases it be described by stating its specific gravity and the temperatures between which it distills.

RAPID METHOD FOR THE DETERMINATION OF MATERIAL IN BITUMINOUS ROAD COMPOUNDS INSOLUBLE 'IN COLD CARBON DISULPHIDE.

For rapid work the committee suggests the following method as a convenient one to be employed. It is based in general upon the standard method, and is applicable to practically all bituminous compounds.

From one to ten grams of the water-free material (depending upon the amount of bitumen present) is weighed into a 150-cc. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 cc. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside for not less than fifteen hours. At the end of this time the contents of the flask are decanted off upon a

weighed Gooch crucible fitted with a long-fiber amphibole asbestos filter. The residue remaining in the flask is then washed with 50 cc. of carbon disulphide, allowed to settle, and decanted as before, the insoluble matter being finally brought upon the filter and washed with 100 cc. of carbon disulphide, or until the washings are practically colorless. The filter and contents are then dried at 125° C., cooled, and weighed. Should any residue remain in the flask, it is also dried and weighed and this weight added to that of the residue in the crucible. The filtrate should be burned off and ignited to an ash and the weight of the ash thus obtained added to that of the insoluble residue. The weight of the total residue deducted from that of the original material gives the weight of bitumen soluble in cold carbon disulphide. In case of tars and pitches the percentage of insoluble residue, determined as above, minus that of any ash which may be found by igniting a separate sample, is reported as free carbon. Glass beads may be employed in the flask, as described in the standard method for the determination of bitumen. This test shall be carried on at a temperature of from 20° to 25° C.

METHOD FOR THE DETERMINATION OF THE CONSISTENCY OF BITUMEN.

The consistency, or penetration, of a bitumen shall be the distance, expressed in hundredths of a centimeter, that a No. 2 needle will penetrate into it at 25° C. (77° F.), in five seconds of time, under a weight of 100 grams, the needle to penetrate direct without friction.

METHOD FOR THE DETERMINATION OF THE LOSS ON HEATING OF OIL AND ASPHALTIC COMPOUNDS.

The loss on heating of oil and asphaltic compounds shall be determined in the following manner: Fifty grams of the water-free material shall be placed in a circular tin box with vertical

sides, measuring about one inch in depth by two and three-eighths inches in diameter, internal measurement. The penetration of the material to be examined shall, if possible, be determined at 25° C., in the manner heretofore described, and the exact weight of the sample ascertained. The sample in the tin box shall then be placed in a hot air oven, heated to 170° C., and kept at this temperature for five hours. At no time shall the temperature of this oven vary more than 2° C. from 170° C. When the sample is cooled to normal temperature, it shall be weighed and the percentage of loss by volatilization reported. The penetration of the residue shall then, if possible, be determined at 25° C., in the manner heretofore described, and the loss in penetration determined by subtracting this penetration from the penetration before heating.

METHOD FOR THE DETERMINATION OF RESIDUAL COKE IN BITUMINOUS COMPOUNDS.

This determination shall be made according to the method described for coal in the Journal of the American Chemical Society, 1899, Vol. 21, page 1116. This method is as follows: Place 1 gram of pure bitumen, free from water, in a "platinum crucible weighing 20 to 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cms. above the top of the burner. The flame should be fully 20 cms. high when burning free, and the determination should be made in a place free from drafts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon."

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100 per cent with the volatile hydrocarbons, excluding the inorganic matter.

METHOD OF SIZING AND SEPARATING THE AGGREGATE IN ASPHALT PAVING MIXTURES.

The method consists of passing the mineral aggregate through several sieves of the following sizes:

| | | | | | | | Diamete | er, in inches. |
|----------|--------|-----|--------|-------|--------|---------|---------|----------------|
| 10 | meshes | per | linear | inch, | size o | of wire | | 0.027 |
| 20 | " | 66 | | " | " | " | | 0.0165 |
| 30 | " | " | " | " | " | " | | 0.01375 |
| 40 | 66 | " | " | " | 66 | " | | 0.01025 |
| 50 80 | " . | " | 66 | . 66 | 66 | 66 | | 0.009 |
| 80 | " | " | 66 | 66 | " | " | | 0.00575 |
| 100 | " | " | 66 | " | 66 | " | | 0.0045 |
| 200 | 44 | " | " | " | " | " | | 0.00235 |

American Society of Civil Envineers

weighed Gooch crucible, fitted with an aspessos pau, urying to constant weight, and weighing the insoluble residue; then igniting crucible until all carbon is burned off, weighing the residue (ash). The difference between the second and third

sides, measuring about one inch in depth by two and threeeighths inches in diameter, internal measurement. The penetration of the material to be examined shall, if possible, be determined at 25° C., in the manner heretofore described, and the exact weight of the sample ascertained. The sample in the tin box shall then be placed in a hot air oven, heated to 170° C., and kept at this temperature for five hours. At no time shall the temperature of this oven vary more than 2° C. from 170° C. When the sample is cooled to normal temperature, it shall be weighed and the percentage of loss by volatilization reported. The penetration of the residue shall then, if possible, be determined at 25° C., in the manner heretofore described, and the loss

ERRATA.

Page 379, for revised methods adopted by the Special Committee on Bituminous Materials for Road Construction, read:

"Revised methods proposed by the Special Committee on Bituminous Materials for Road Construction."

cent with the volatile hydrocarbons, excluding the inorganic matter.

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| | | | | | | | | Diameter, in inches. |
|-----|--------|-----|--------|-------|------|----|------|----------------------|
| 10 | meshes | per | linear | inch, | size | of | wire | 0.027 |
| 20 | 66 | 66 | | 44 | " | | " | 0.0165 |
| 30 | 44 | 66 | " | 46 | " | | 66 | 0.01375 |
| 40 | 66 | 66 | 66 | 66 | 66 | | 66 | 0.01025 |
| 50 | " | 66 | 66 | - 66 | 66 | | | 0.009 |
| 80 | 66 | " | 66 | 66. | 66 | | | 0.00575 |
| 100 | 66 | " | 66 | " | 66 | | | 0.0045 |
| 200 | 68 | 66 | 66 | 66 | " | | " | 0.00235 |

American Society of Civil Engineers

REVISED METHODS ADOPTED BY THE SPECIAL COMMITTEE ON BITUMINOUS MATERIALS FOR ROAD CONSTRUCTION.

W. W. CROSBY, Chairman.

A. H. BLANCHARD, Secretary.

TARS.

Water-Soluble Materials.— Boil gently two grams of material with 25 cc. of distilled water for one hour. Filter and wash with 25 cc. of boiling water. Evaporate filtrate in weighed dish to dryness and constant weight at 105° C. Weigh residue. Ignite residue and weigh again, giving weight of inorganic matter plus weight of crucible. Weight No. 2 minus weight No. 3 gives weight of organic matter.

Specific Gravity. — Use some standard form of pycnometer. Material and distilled water must have a temperature of 25° C. For semisolid and solid materials use Sommer's pycnometer.

Free Carbon. — The free carbon shall be determined by dissolving for fifteen hours two grams of the compound in 100 cc. of cold carbon bisulphide, filtering the solution through a weighed Gooch crucible, fitted with an asbestos pad, drying to constant weight, and weighing the insoluble residue; then igniting crucible until all carbon is burned off, weighing the residue (ash). The difference between the second and third

weights is "free carbon." The difference between first and third is ash, which should be noted.

Fixed Carbon. — About one gram of the compound is weighed into a platinum crucible one and one-eighth to one and one-half inches high. The crucible with the lid on is heated, first gently, and then until no more smoke and flame issues between the crucible and the lid. It is then heated three and one-half minutes in the full heat of the burner; then cooled and weighed. The crucible lid is then removed and the crucible and contents allowed to remain in the full heat of the burner until the carbon is burned off, and then weighed again. The difference between these two weights is the fixed carbon.

Evaporation. — Twenty grams of compound are heated in a flat-bottomed dish, two and one-half inches in diameter and about one inch high, for a total of five hours in three successive periods of three, one and one hours, respectively, in an oven, the interior of which is maintained at a uniform and constant temperature of 170° C. This oven is to be controlled by any thermo regulator, controlling within two degrees, and is to have its full temperature before the compound is introduced. The dish must be level. Remove dish from oven and stir contents thoroughly for one minute between successive periods.

Penetration of Residue from Evaporation Tests. — The penetration shall be measured by a standard machine using 100 grams load and No. 2 needle. Use a flat-bottomed glass dish seven-eighths of an inch in diameter and one and one-half inches in height. Fill flush with top with material and allow same to stand at room temperature for one-half hour. Immerse in water bath, covering material for one hour. Immerse needle to be used for five minutes in same bath. Test at once, making three determinations. The recorded penetration will be the average value. Temperature 4° C. and 25° C.

(Note): Residue must be melted at lowest possible temperature and thoroughly mixed in by stirring.

Melting Point of Residue from Evaporation. — The material whose melting point is to be determined is melted and poured into a mold that will make a one-half inch cube. A No. 10 gauge wire about six to eight inches long is bent at right angles for a length of three-quarter inch at one end and the center of the cube is placed on this end so that one of the diagonals of the vertical face of the cube is parallel to the long part of wire. Take a bottle of a size about two inches in diameter and four inches high and place a piece of white paper in the bottom of it. Pass the long part of the wire through the cork of the bottle so that the lower edge of the cube will be within one inch of the bottom of the bottle. Also put a thermometer through the cork so that the bulb is opposite the cube. Place the bottle in a water or oil bath and raise the temperature of the bath at a rate of three to six degrees C. a minute. The melting point of the material is the temperature of the thermometer inside the bottle at the time that the material touches the paper in the bottom of the bottle.

Distillation. —

Up to 105° C.

From 105° to 170° C.

From 170° to 225° C.

From 225° to 270° C.

From 270° to 300° C.

Seven hundred grams of the compound are weighed into a retort (E. & A. four pints No. 4521), whose top is fitted with a tee as close as possible to the retort, and a condenser pipe twenty-four to thirty-six inches_long; the upper branch of the tee is used for the insertion of a thermometer, the top of whose bulb is placed immediately below the main outlet, of the tee.

Viscosity or Consistency. — Temperatures at which viscosities will be determined are 100° C. and 25° C.

Penetrometer to be used in accordance with standard method on materials solid at above temperatures. On materials which at the above temperature the penetrometer cannot be used, the viscosity shall be determined by one of the following instruments:

Engler Viscosimeter.

Lunge Tar Tester.

New York Testing Laboratory Viscosimeter.

COMPOUNDS PREPARED FROM PETROLEUM OR NATURAL ASPHALT PITCHES.

Melting Point of Solid Asphalts.— Same method as for residue from evaporation of tars.

Water-Soluble Materials. — Same method as for tars.

Specific Gravity. — Same method as for tars.

Free Carbon. — Same method as for tars.

Material Soluble in Cold Carbon-Tetrachloride. — Same method as for free carbon, except carbon-tetrachloride is used as a solvent instead of carbon-bisulphide.

Fixed Carbon. — Same method as for tars.

Paraffin. — One hundred grams or less of the compound is distilled rapidly in a retort to dry coke.

Five grams of the well mixed distillate is treated in a twoounce flask with 25 cc. Squibbs absolute ether; after mixing thoroughly, 25 cc. Squibbs absolute alcohol is added and the flask packed closely in a freezing mixture of finely crushed ice and salt for at least 30 minutes. Filter the precipitate quickly by means of a suction pump, using a No. 575 C. S. & S. 9 c.m. hardened filter paper. Rinse and wash the flask and precipitate (with 1 to 1 Squibbs alcohol and ether mixture cooled to —17° C.) until free from oil (50 cc. of washing solution is usually sufficient). When sucked dry remove paper, transfer waxy precipitate to small glass dish, evaporate on steam bath and weigh paraffin remaining on dish.

Calculation. — Weight of paraffin divided by weight of distillate taken and multiplied by per cent of total distillate used from original sample, equals per cent of paraffin.

Evaporation Test No. 1. — Same method as for tars.

Penetration of Residue from Evaporation Test No. 1. — Same method as for similar residue of tars.

Melting Point of Residue from Evaporation Test No 1. — Same method as for similar residue of tars.

Solubility in 88° Baume Naphtha. — Two grams of compound are placed in four-ounce oil sample bottle made up to 100 cc. with 88° B. naphtha, having a boiling point between 40° C. and 55° C., the whole well shaken until compound is broken up. The bottle is then centrifugalized for ten minutes, 50 cc. are withdrawn into a weighed flask, the naphtha distilled by a water bath and the residue weighed. Another ten cc. of the naphtha solution is run over three and one-half inches Petri glass and allowed to evaporate for twenty-four hours at room temperature. Note character of residue, i.e., sticky or oily.

Viscosity or Consistency. — Same as for tars.

Evaporation Test No. 2. — Same method as for tars except oven temperature shall be 205° C.

Penetration of Residue from Evaporation Test No. 2. — Same method as for tars.

Melting Point of Residue from Evaporation Test No. 2. — Same method as for tars.

CHAPTER XV

SELECTION OF DUST PREVENTIVES AND ROAD BINDERS.

Most of the factors which should govern the selection of dust preventives and road binders have at one time or another been discussed in previous chapters, but so many instances have come under the author's notice where failures have resulted from the exercise of poor judgment in selection, that it seems well to close this book with a short chapter on this most important subject. It is undoubtedly true that thousands of dollars are wasted annually in a repetition of experiments which time and again have proved costly mistakes. On the other hand experiments which have given good results in some places have also proved failures when tried in different localities. The whole subject is as yet in an experimental stage and much confusion has arisen over the contradictory results obtained by various experimenters working with apparently the same material. There would seem to be three main factors to be considered in this connection, any one of which might account for such discrep-They are: ancies.

- (1) Differences in the physical and chemical characteristics of materials which are sold under the same trade name or which are known only as types.
 - (2) Differences in methods of application.
- (3) Differences in local conditions, to which the roads are subjected.

It is of course evident that the road builder has no control over local conditions to which a road is subjected, but in the selection and application of the binding medium to meet these conditions he should exercise considerable judgment. Close observation and practical experience have convinced the author that certain fundamental principles have generally been over-

looked or disregarded in this connection, and that this is the cause of a large percentage of failures. It is necessary, therefore, that not only the experience of others be considered, but that some thought be given to the probable effect of local conditions upon the results which have in general been obtained. The importance of ascertaining the composition and quality of the material has already been dwelt upon at some length, but while these are most important points, they are not the only ones to be taken into account, and it will be found that differences in local conditions are factors of too much importance to be disregarded. Great differences in conditions have of course generally been considered, but it is not always those clearly apparent that cause the greatest variance in results. It is this fact that makes it impracticable to frame satisfactory specifications which may be considered as standard for even a single individual type of binder, to be applied in a given manner.

Owing to lack of sufficient data by experimenters, it is often a hard matter to correlate the results obtained in practice to their actual causes, but certain facts are indicated which if properly considered should be of some value to the experimenter who has not already learned by experience what material is best suited for the road he has occasion to treat. It is the author's purpose here to present these facts in such form as to serve as a general guide in the selection of material, but it should be understood that they are of use as a guide only and in no sense are to be considered as hard and fast rules. In many instances the selection of a road binder may be influenced by a combination of conditions which would be impossible to foresee except in individual cases. Sometimes a choice may seem to be equally divided among a number of materials, and experiment alone will determine which, if any, is the most suitable. In many cases the experimenter is handicapped by lack of funds, so that the most suitable material cannot always be obtained. In these cases a less suitable material will have to be employed, although in the long run this will often prove more costly. Except in rare instances economy is the most important point to be considered

and while permanency of results is often synonymous with economy it is not always so.

The division of dust preventives and road binders into three classes, temporary, semipermanent and permanent, suggests in a general way the first point that should be considered in regard to selection. Taken in connection with the three great classes of roads, county, suburban and city, it is at once evident that under ordinary conditions only the semipermanent and permanent binders are suited to the first of these for the reason that it is impracticable to treat long stretches of country road at comparatively short intervals of time. When employing temporary binders the road should not only be under constant observation, so that applications may be made whenever necessary, but facilities should be such that the work may be quickly and efficiently performed. It is seldom that this condition of affairs exists on a country road. With respect to suburban and city roads and streets, however, no such restrictions exist in the majority of cases, and any or all classes of binders may be selected.

Selection of Materials for Treating Country Roads. — Country roads may be divided into two general classes, hard and soft roads. The first class is represented by the macadam and other broken-stone roads and the second by earth roads. Sand and gravel roads may also be included in the latter class, although in many cases they more nearly approach the broken-stone roads in point of hardness. In the case of hard roads a choice of either oil or tar products will exist, but in the treatment of soft roads oils only have so far proved successful, and except for purely experimental purposes the choice is limited to this class of material.

The selection of a binder for use on a rural macadam road will depend upon several conditions. The first of these would ordinarily be the relative cost at the given location. Other factors, such as relative quality of the available materials, available apparatus for applying same, funds available for treatment, climatic conditions, condition of the road, character of the road stone, and amount and quality of traffic to which the

road is subjected, should also be taken into account and the method of application with reference to these conditions should be carefully considered. In view of the fact that most work of this kind has not been planned or carried out with sufficient forethought, a hypothetical example may be considered, even at risk of entering into too great detail. The necessity of clearly illustrating this matter has been made evident to the author, not only from reviewing published descriptions of experiments, but from actual work along these lines.

For example, let us suppose that a stretch of rural macadam is to be treated with regard to dust suppression. Our first effort would be to determine if possible any one predominant cause for excessive dust formation. Upon investigation we might find that the road stone showed no cementing qualities, and if the road was exposed to but little motor traffic a top dressing of some good binding rock screenings might solve the problem quite satisfactorily. On the other hand, if motor traffic was heavy we should have to resort to the use of a special binder, as no stone road has so far proved able to successfully withstand the action of heavy mixed traffic. With regard to a choice of these materials we should first ascertain which is most readily available at a reasonable cost. If a refined tar produced at a low temperature and containing a fair amount of good pitch base could be obtained it might be tentatively chosen. In some localities an asphaltic or semiasphaltic oil might be more readily available, or a residual oil preparation, but in any event we should ascertain in so far as possible the particular properties of the material which we are considering and unconditionally reject those which, for reasons that have already been discussed, are almost sure to prove unsatisfactory. Thus a high carbon tar, a paraffin, petroleum or a badly cracked residuum would be at once discarded, no matter how cheap or readily available it might be.

If climatic conditions were such that a surface application would be unlikely to last throughout the winter, and we were unable to rebuild the road so as to make it a bituminous macadam, it would prove most economical to apply only sufficient material to last throughout the dusty season. In this case a cold application of coal tar diluted with sufficient water gas tar or oil tar to give it the proper fluidity might be made, or a crude semiasphaltic petroleum used in preference to a more expensive residuum or cut back product. In climates where a long succession of alternate frosts and thaws occur throughout the winter, accompanied by cold rains, a treatment of this sort will prove far less expensive than a surface application of heavier binding material. Under more favorable conditions, however, this would not be true, and applications of tar or oil requiring heat might be more economical. conditions of the road will often indicate the method of treatment and kind of material which should be employed. If the road is in fairly good condition a surface application is often all that is required. Where the road is badly torn up and ravelled, however, it will often prove better policy in the long run to reconstruct it with the addition of a bituminous matrix or else to resurface it with a heavy coat of bitumen covered stone. In a case of this sort a good refined tar is to be preferred unless a very heavy semiasphaltic or asphaltic oil can be secured. either material can be obtained the character of the road stone may decide in favor of one or the other. A hard but somewhat porous rock is to be preferred in either case, but perhaps more particularly in that of tar, which is less easily absorbed than oil.

The choice of binders for soft country roads is somewhat restricted, owing to the fact that oil only can be employed. For the softer roads an oil containing even a relatively small amount of paraffin base is valueless as a permanent binder, and we are thus narrowed down to a choice between the exceptionally good semiasphaltic oils, the true asphaltic oils and the residuums and cut back products obtained from each. That oil containing the greatest amount of asphaltic base is usually to be preferred, although not always. In the case of ordinary earth, clay or loam roads the presence of a greater amount of true oil is required than in that of sand and gravel

roads, in order to prevent the surface from becoming powdery under the action of traffic. Badly cracked residuums should be avoided, even to the extent of using a crude oil containing less asphaltic base. A very clayey soil should be modified by the addition of sand before treatment, and as has been noted, measures should be taken to overcome the effect of alkali soils upon the oil used. Methods of application suitable to various conditions have been discussed elsewhere and need not be considered here. Where gravel roads are to be treated it is not always necessary to employ an extremely heavy asphaltic oil, although such a material is to be preferred. Where fairly heavy crude semiasphaltic or residual oils can be obtained at a low figure they may often be used to advantage. And while the results may not be quite so permanent the reduction in cost as compared with the truly asphaltic oils will, under present conditions, more than compensate this difference, especially in our eastern states.

Where it is decided to construct an earth road with an oil binder, it would for most cases be bad practice to select a fluid semiasphaltic oil residuum containing no appreciable amount of volatile oils, and yet this is often done. The author has in mind an instance where such an oil was selected for this purpose and first applied at the rate of one gallon per square yard to the depth of six inches in a very approved manner so far as incorporating the binder with the earth was concerned. The results were somewhat disappointing to the experimenter, although exactly what should have been expected from such a product. The oil being very fluid was completely absorbed by the earth, and as it had but little original binding value and was incapable of improving in this respect, no visible effect was produced other than that the road became somewhat less dusty and its color was made slightly darker. The experimenter rightly inferred that sufficient binder had not been employed and decided to apply another gallon per square yard. He made the mistake, however, of again using the same fluid residuum. This time the road was made absolutely dustless, but it was soft and mealy and refused to bond and consolidate under the roller. It also showed signs of sweating under the action of sun and traffic. This should have been a warning, but as the road had not bonded satisfactorily he thought that perhaps an additional gallon of oil per square yard would put it in good condition. The third gallon was, therefore, applied, but the soil having become practically saturated with the first two applications refused to take up the third, and sweated so badly that the surface became soft and gummy, the oil was tracked by pedestrians, spattered upon vehicles and their occupants and in fact became a general nuisance, which was a hundredfold worse in wet weather. It was then thought that the application of broken stone might remedy the trouble. Accordingly two or three inches of number two crushed stone were applied and rolled into the road. The stone was pushed out of sight just as though it had been laid upon a wet clay foundation, and the supersaturated oiled earth coming to the top produced the same condition of affairs as before. Eventually the whole surface had to be removed and replaced with clean broken stone.

This is only a single example of what has happened many times, but serves to show how experience is dearly paid for. this particular instance the author was called upon to examine a sample of the oil which had been used. He found it to be a rather poor grade of semiasphaltic fluid residuum totally unfit for any kind of road use except perhaps as a dust palliative when applied in very small quantities to a macadam surface. general appearance of the oil ought almost to have been sufficient evidence of its unfitness for use in road construction, but a few simple tests, such as the loss by volatilization at 163° C., naphtha insoluble bitumen, fixed carbon determinations, etc., together with a written explanation, proved conclusively to the experimenter the cause of failure. Since then he has had each lot of road binder which he has used examined to determine its fitness to meet given conditions and is no longer dependent upon the word of the manufacturer or sales agent as to the quality of material which he purchases.

Selection of Materials for Treating Suburban Roads. — A wider selection of dust preventives and binders is possible in the treatment of suburban than in country roads. Here all types of road binders may compete, and it is often a difficult matter to choose the best material. As a rule, hard roads predominate in suburban districts and it is mainly the selection of material for the treatment of these with which we shall have to deal. The hard roads, which are for the most part macadam, may be considered under two divisions, according to the amount of traffic they receive, i.e., those which carry light traffic, and those which carry heavy traffic. In either case the automobile must be taken into account and the road treated accordingly. The surface application of a semipermanent binder in moderate quantity will usually prevent dust formation quite satisfactorily upon roads which are not subjected to an excessive amount of traffic, but the same will not necessarily hold good for heavily traveled roads. Here, as in all cases, cost will prove a most important factor. When the first expense can be met, a well-constructed bituminous macadam will often prove the most economical in the long run, but even then the application of temporary binders may be required to lay the dust if much is carried upon the road from outside sources. As the conditions governing the selection of permanent binders have already been mentioned under country roads, it is only necessary here to consider those conditions influencing the selection of temporary binders, should a choice in their favor be made over the permanent binders.

If a system of hydrants be located at convenient distances along the road, salt solutions, emulsions, or waste sulphite liquors can be easily employed; if not, recourse must be had to one of the lighter oil or tar products. In the latter case that product which contains the greatest amount of binding base per unit cost should be selected unless it possesses other qualities which are particularly undesirable, such as a strong and disagreeable odor. If an emulsion or salt solution can be employed, the character of the road material may determine which is the more suitable. Thus a hard road, on which the products of wear will be slight provided they are retained upon the surface, or one in which the cementing value of the rock dust is good, can be effectively treated with a solution of some salt such as calcium chloride. Also in cases where the climate is more or less humid a deliquescent salt may give the most satisfactory results. When the climate is very arid, however, the salt will have to be fed with too many applications of water to make its use economical. In the case of a road built of very soft rock which wears badly under traffic, the asphaltic oil emulsions are to be preferred on account of the binding and road building qualities which they possess. As a general rule, when it is particularly desirable to obtain a road building emulsion, one containing a volatile saponifying agent might be selected in preference to the non-volatile saponifiers, especially in the case of an asphaltic oil product where the binding base is apt to be permanently injured by the presence of fixed alkalies. choice of other emulsions and light preparations will in many cases depend upon locality. Where waste products of a deliquescent or binding character can be obtained, they may be utilized for the purpose of dust laying and are apt to be cheaper than any other material in localities near which they are produced.

Selection of Dust Preventives for Use in Towns and Cities. — In cities and towns where the traffic is heavy and of a mixed character, true paving materials should undoubtedly be selected for construction work, but unless their use is supplemented by that of the surface application of temporary binders dust prevention is almost an impossibility. This is to a great extent due to the fact that large quantities of dust from outside sources are brought upon the streets, which makes it necessary to apply the dust preventives at frequent intervals. As the semipermanent liquid binders in concentrated form cannot be applied in this manner for obvious reasons, recourse must be had to the temporary binders or dust palliatives.

In the class of pavement having a smooth, unbroken and resilient surface, such as sheet asphalt, conditions more closely approach the ideal dustless pavement than any other so far devised. The products of wear are comparatively small in quantity and there are few cracks or crevices where dust can accumulate, and yet they are by no means dustless, — unless kept free from dirt and refuse by frequent cleanings. As this type of pavement is practically impervious, no great amount of dust preventive will be absorbed if any is used and most of it will be removed when the street is cleaned unless it has already volatilized. Any non-volatile dust layer is apt to make the pavement slippery, and volatile materials evaporate so rapidly in hot weather that except for laying the dust just previous to sweeping they are of little value. Water is about the only material that seems to be suitable for this class of pavements.

Brick pavements, stone block pavements and, in fact, any pavements which present a less sheet-like surface than the asphalt type can be more satisfactorily treated for dust prevention. On these pavements dust tends to accumulate in the crevices between the bricks or blocks and in moderate quantities is almost unnoticeable until raised by winds or traffic. An apparently clean street will, therefore, often prove to be a very dusty one. The use of a temporary binder to saturate this dust and hold it down until cleaning becomes necessary can be managed economically, as any dust preventive that is applied will have a natural tendency to collect in just those portions of the road where the dust has accumulated and if used in moderate quantity should not produce the undesirable conditions resulting from similar applications upon an asphalt pavement. Solutions of calcium chloride should prove satisfactory for this work. but the best form of temporary binder for any particular pavement will in most cases have to be determined by experiment.

Selection of Materials for Treating Park Roads. — Before leaving the subject of selection, a few words may not be amiss in relation to city park roads. Here under ordinary circumstances conditions are somewhat different from those pertaining to any of the three classes so far considered. In the first place park roads are almost entirely given over to pleasure traffic.

As they are subjected to little or no heavy teaming, they are usually of lighter construction than the ordinary road and in many cases are composed of rather soft material. Motor traffic is likely to be excessive and some suitable dust preventive is often needed.

Semipermanent binders may be used to advantage in many cases, but as a general rule more economical and satisfactory results can be obtained with temporary binders. Soap solutions or emulsions of asphaltic or semiasphaltic oils have given good results at small expense in a number of instances where emulsifying plants have been established in or near the park. Other forms of emulsions as well as salt solutions have also proved effective, but usually at a somewhat greater cost. When soap emulsions of oil are employed, it is necessary to give the road more attention than when heavier binding emulsions are used, especially in cases where considerable loose material occurs upon the road. The reason for this has already been considered and it is only necessary to add that it does not constitute a serious objection when applied to park roads, as facilities are usually such that the work can easily be handled. A choice between permanent, semipermanent and temporary binders for use on park roads may depend upon any one or more of the conditions already mentioned for the various other classes of roads, but in particular where dust from outside sources is likely to be carried upon the road in considerable quantity, the temporary binders are to be preferred to the semipermanent.

Specifications for Road Binders. — The author has been repeatedly asked to furnish specifications for road binders, the prevailing idea among road engineers seeming to be that a standard set of specifications should be formulated which would always insure satisfactory results. To those who have read this book it must appear evident that this is practically an impossibility. No one set of specifications of any value can ever be made to cover all varieties of road binders. Even for a single type the factors which control selection must of necessity control specifications and it has been shown that these factors are

exceedingly variable. Such considerations will always make the framing of specifications a matter of expert opinion for individual cases.

Where the desired method of application, character of the road, and local conditions to which it is subjected are known, a working basis is established for the formulation of specifications for a given type of binder. If any one of these three factors is unknown, however, there can be no guarantee that a satisfactory material will be furnished under specifications.

Owing to the fact that standard methods of examination have not been generally adopted, it is at present advisable to describe the desired methods in any set of specifications which may be framed, as otherwise they may become a matter of controversy. The following specifications will perhaps serve as a general guide or form for both tar and oil products which are to be used for specific purposes. It should be understood, however, that the values assigned are subject to change to meet local conditions.

The tar specifications given below are framed to secure a suitable product for use according to the penetration method in a southern locality. This product may be prepared by the distillation of either a water gas tar, a low or medium carbon coal tar or a properly controlled mixture of water gas tar and coal tar. The methods of examination required to determine the specified qualities are described in Chapter XIII.

SPECIFICATIONS FOR ROAD TAR.

TO BE USED ACCORDING TO THE PENETRATION METHOD IN THE CONSTRUCTION OF TAR MACADAM ROADS IN......COUNTY, STATE OF.....

- (1) The tar shall have a specific gravity of not less than 1.170 nor greater than 1.250 at 25° C.
- (2) It shall be soluble in c.p. carbon bisulphide at air temperature to at least 80 per cent and shall contain not over 20 per cent free carbon, preferably much less.

- (3) Upon ignition it shall show not over 0.5 per cent inorganic residue.
- (4) When a sample of the tar is subjected to the float test, the float shall sink in water maintained at 50° C. in not less than two and one-half minutes nor more than three minutes.
- (5) When 250 cc. of the tar is distilled in a 750 cc. glass retort at a rate not exceeding two drops of distillate per minute, the total distillate to 170° C. as registered by a thermometer whose bulb is level with the bottom juncture of stem and body of the retort shall not exceed 2 per cent by volume of the original material. The total distillate to 270° C. shall in no case exceed 50 per cent, and when the tar contains more than 10 per cent free carbon, this distillate shall not exceed 40 per cent by volume of the original material.
 - (6) The tar shall be free from water upon delivery.

It may be noted with reference to the individual clauses that.

- (1) The lower limit for specific gravity together with clause (3) insures a tar product, and to a certain extent controls the consistency of a very low carbon tar. The higher limit controls the consistency of a tar containing the maximum free carbon contents, and together with clause (4) reinforces clause (2).
- (2) This clause is worded so as to control the free carbon contents as determined according to any method, and specifically by its solubility in carbon bisulphide.
- (3) The relation of this clause to clause (1) has been described. It further prevents the adulteration of the tar with any inert mineral matter.
- (4) Compliance with the float test insures the desired consistency within comparatively narrow limits for tars of different free carbon contents and very definitely for duplicate lots of tars containing the same percentage of free carbon.
- (5) This clause insures what is considered to be a normal relation between distillates, both volatile and non-volatile, and residue, for tars which contain a relatively large amount of

naphthalene. If the absence of appreciable quantities of naphthalene had been specified, the allowable limit of total distillate below 270° C. might have been somewhat lower, without danger of the tar becoming rapidly brittle under service conditions. This clause also insures a refined product.

(6) Absence of water insures a refined product and prevents carelessness in the preparation of the tar in so far as condensation is concerned if the distillation is carried on by means of steam. This specification also averts trouble due to frothing when the tar is heated during application.

An oil product to be used

ERRATUM.

Page 396, line 7, the word "minute" should read "second."

⁽⁴⁾ When tested for 5 seconds at 25°C. with a standard No. 2 needle weighted with 100 grams, it shall show a penetration of not less than 15.0 mm., nor greater than 25.0 mm. unless the residue obtained from the volatilization test (see clause 5) shows a penetration of not over 20.0 mm. when tested in the manner above described.

⁽⁵⁾ When 20 grams of the material is heated for 5 hours in a cylindrical tin dish approximately two and one-half inches in diameter by one inch high at a constant temperature of 163° C.,

- (3) Upon ignition it shall show not over 0.5 per cent inorganic residue.
- (4) When a sample of the tar is subjected to the float test, the float shall sink in water maintained at 50° C. in not less than two and one-half minutes nor more than three minutes.
- (5) When 250 cc. of the tar is distilled in a 750 cc. glass retort at a rate not exceeding two drops of distillate per minute, the total distillate to 170° C. as registered by a thermometer whose bulb is level with the bottom juncture of stem and body of the retort shall not exceed 2 per cent by volume of the original material. The total distillate to 270° C. shall in no

scribed. It further prevents the adulteration of the tar with any inert mineral matter.

- (4) Compliance with the float test insures the desired consistency within comparatively narrow limits for tars of different free carbon contents and very definitely for duplicate lots of tars containing the same percentage of free carbon.
- (5) This clause insures what is considered to be a normal relation between distillates, both volatile and non-volatile, and residue, for tars which contain a relatively large amount of

naphthalene. If the absence of appreciable quantities of naphthalene had been specified, the allowable limit of total distillate below 270° C. might have been somewhat lower, without danger of the tar becoming rapidly brittle under service conditions. This clause also insures a refined product.

(6) Absence of water insures a refined product and prevents carelessness in the preparation of the tar in so far as condensation is concerned if the distillation is carried on by means of steam. This specification also averts trouble due to frothing when the tar is heated during application.

An oil product to be used under similar conditions according to • the penetration method might be required to show the following properties:

SPECIFICATIONS FOR ROAD OIL.

- TO BE USED ACCORDING TO THE PENETRATION METHOD IN THE CONSTRUCTION OF OIL MACADAM ROADS IN COUNTY, STATE OF
- (1) The oil shall have a specific gravity not greater than 1.05 and not less than 0.98 at 25° C. unless the residue obtained from the volatilization test (see clause 5) has a specific gravity of not less than .985.
- (2) It shall be soluble in c.p. carbon bisulphide at air temperature to at least 99 per cent and shall contain not over 0.3 per cent organic matter insoluble.
- (3) It shall contain not less than 12 per cent nor more than 25 per cent of bitumen insoluble in 86° B. paraffin naphtha at air temperature.
- (4) When tested for 5 seconds at 25°C. with a standard No. 2 needle weighted with 100 grams, it shall show a penetration of not less than 15.0 mm., nor greater than 25.0 mm. unless the residue obtained from the volatilization test (see clause 5) shows a penetration of not over 20.0 mm. when tested in the manner above described.
- (5) When 20 grams of the material is heated for 5 hours in a cylindrical tin dish approximately two and one-half inches in diameter by one inch high at a constant temperature of 163° C.,

the loss in weight by volatilization shall not exceed 20 per cent. The residue remaining shall show a penetration of not less than 10.0 mm. nor greater than 20.0 mm. when tested in the manner hereinbefore described.

- (6) Its fixed carbon shall not be less than 6 per cent nor greater than 20 per cent.
 - (7) The oil shall be free from water upon delivery.

With reference to these clauses it may be said that:

- (1) The specific gravity limits, together with clause (2) eliminate all of the very fluid oils, at the same time making allowance for cut-back products whose specific gravities may be low, owing to the presence of light volatile fluxes. The upper limit eliminates tar products but also the presence of some of the solid native bitumens. If it is desired to include the latter class of materials, the clause should be made to apply only to the bitumen free from mineral matter.
 - (2) This clause insures a very pure bitumen practically free from mineral matter. If it is desired to include products prepared from such materials as Trinidad asphalt, allowance should be made for considerable quantities of mineral matter and a larger amount of insoluble inorganic matter. The specification would then, however, include oil products which might be adulterated with inorganic material.
 - (3) This clause aims to secure a certain degree of stability in the material, due to the presence of asphaltic hydrocarbons. The highest limit provides against excessive blowing in the process of manufacture and to some extent against a tendency toward extreme lack of ductility.
 - (4) The penetration specification provides for the proper consistency both of residual and cut-back products, for the particular class of work under consideration.
 - (5) This clause reinforces clause (4) and insures that the material will attain but not exceed the necessary degree of hardness under service conditions. At the same time it provides against excessive loss by volatilization.

(6) This clause reinforces clause (3) and eliminates the truly paraffin materials.

(7) This clause prevents frothing when the material is heated. Summary and Conclusions. — In this chapter the author has attempted by a general discussion of the subject of selection and the consideration of a few specific cases to develop the principles which should govern the selection and specification of dust preventives and road binders. It has been possible to do this in only a very limited way, owing to the great number of factors which may modify selection. Local conditions to which a road is subjected have been shown to comprise some of the most important of these factors but the primary purpose for which any material is employed should never be lost sight of. Thus for dust prevention only a temporary binder or palliative may be employed, but never with the expectation that it will serve as a permanent binder. On the other hand, the permanent binders, while of great value as dust preventives so far as the wear of the road is concerned, cannot be expected to serve indefinitely as dust layers. Other considerations which may govern selection are cost, ease of application, imperviousness, time required before traffic can be admitted to the road after treatment, freedom from harmful and offensive qualities, slipperiness, etc. It should be remembered, however, that, no matter how much care and attention is paid to selection, unless the material is properly applied and the road in proper shape to be treated, satisfactory results will not be obtained. Moreover, the necessity for careful and constant maintenance should never be forgotten if the work is to be put upon the most economical basis possible. Such aids to dust prevention and road preservation as mentioned in Chapter I will also be found serviceable in cases where they can be utilized.

APPENDIX

COMPARISON OF DEGREES BAUMÉ AND SPECIFIC GRAVITY. (Liquids lighter than water.)

(1) Sp. gr. =
$$\frac{140}{130 + {}^{\circ}\text{B\'e}}$$
 at 17.5°C

(2)
$$^{\circ}$$
B = $\frac{140}{\text{Sp. gr.}}$ - 130 at 17.5°C.

| ° Bé. | Sp. Gr. | ° Bě. | Sp. Gr. |
|----------|---------|----------------------------|---------|
| 10 | 1.0000 | 46 | 0.7954 |
| II | .9929 | | . 7909 |
| 12 | .9859 | 47 48 | . 7865 |
| 13 | .9790 | 49 | .7821 |
| 14 | .9722 | 50 | .7777 |
| 15 | .9655 | 51 | .7734 |
| 15 16 | .9589 | 52 | . 7692 |
| 17 | .9523 | 53 | .7650 |
| ı8 | .9459 | 54 | . 7608 |
| 19 | .9395 | 54 55 56 57 58 | .7567 |
| 20 | .9333 | 56 | .7520 |
| 21 | .9271 | 57 | . 7486 |
| 22 | .9210 | 58 | . 7446 |
| 23 | .9150 | 59 60 | . 7407 |
| 24 | .9090 | 60 | .7368 |
| 25 | .9032 | 70 | . 7000 |
| 26 | .8974 | 71 | . 6965 |
| 27 28 | .8917 | 72 | . 6931 |
| 28 | .8860 | 73 | , 6896 |
| 29 | .8805 | 74 | . 6863 |
| 30 | .8750 | 75 76 | . 6829 |
| 31 | .8695 | 76 | . 6796 |
| 32 | .8641 | 77 78 | . 6763 |
| 33 | .8588 | 78 | .6731 |
| 34 | .8536 | 79 80 | . 6698 |
| 35 36 | . 8484 | 80 | . 6666 |
| 36 | .8433 | 81 | . 6635 |
| 37 38 | .8383 | 82 | . 6604 |
| 38 | 8333 | 83 84 | .6573 |
| 39 | .8284 | 84 | . 6542 |
| 40 | .8235 | 85 86 | .6511 |
| 41 | .8187 | 80 | . 6482 |
| 42 | .8139 | 87 88 | . 6452 |
| 43 | .8092 | 88 | .6422 |
| 44 | .8045 | 89 | .6393 |
| 45 | .8000 | 90 | . 6363 |

COMPARISON OF DEGREES BAUMÉ AND SPECIFIC GRAVITY.

(Liquids heavier than water.)

(1) Sp. gr. =
$$\frac{145}{145 - {}^{\circ}\text{B\'e}}$$
 at 15.5° C.

(2)
$${}^{\circ}\text{B\'e} = 145 - \frac{145}{\text{Sp. gr.}} \text{ at } 15.5 {}^{\circ}\text{ C.}$$

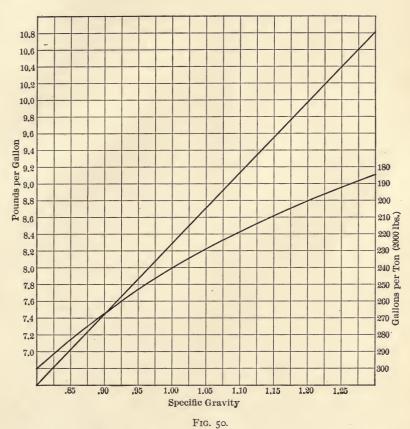
| °Bĕ. | Sp. Gr. | ° Bĕ. | Sp. Gr. |
|----------------------------|---------|----------|---------|
| | | | |
| 0 | 1.0000 | 18 | 1.1417 |
| I | 1.0069 | 19 | 1.1508 |
| 2 | 1.0140 | 20 | 1.1600 |
| 3 | 1.0211 | 21 | 1.1694 |
| 3 4 5 6 7 8 | 1.0284 | 22 | 1.1789 |
| 5 | 1.0357 | 23 | 1.1885 |
| 6 | 1.0432 | 24 | 1.1983 |
| 7 | 1.0507 | 25 26 | 1.2083 |
| | 1.0584 | 26 | 1.2185 |
| 9 | 1.0662 | 27 | 1.2288 |
| 10 | 1.0741 | 28 | 1.2393 |
| · II | 1.0821 | 29 | 1.2500 |
| 12 | 1.0902 | 30 | 1.2609 |
| 13 | 1.0985 | 31 | 1.2719 |
| 14 | 1.1069 | 32 | 1.2832 |
| 15 | 1.1154 | 33 | 1.2946 |
| 16 | 1.1240 | 34 | 1.3063 |
| 17 | 1.1328 | 35 | 1.3182 |

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES.

(1) °F. =
$$\frac{9}{5}$$
 °C. + 32
(2) °C. = $\frac{5}{5}$ (°F. - 32)

(2) °C. =
$$\frac{5 (°F. - 32)}{9}$$

| С. | F. | c. | F. | c. | F. | c | F. | c. | F. | c. | F. |
|----------|--------------|----|-------|----------|-------|-------|----------------|-----|---------------|------|----------------|
| 0 | 32. | 38 | 100.4 | 76 77 | 168.8 | 114 | 237.2 | 152 | 305.6 | | |
| 1 2 | 33.8 | 39 | 104. | 78 | 172.4 | 116 | 240.8 | 154 | 307.4 | 191 | 375.8 377.6 |
| 3 | 37.4 | 41 | 105.8 | 79 | 174.2 | 117 | 242.6 | 155 | 311. | 193 | 379.4 |
| 4 | 39.2 | 42 | 107.6 | 86 | 176. | 118 | 244.4 | 156 | 312.8 | 194 | 381.2 |
| | 41. | 43 | 109.4 | 81 | 177.8 | 119 | 246.2 | 157 | 314.6 | 195 | 383. |
| 5 6 | 42.8 | 44 | 111.2 | 82 | 179.6 | 120 | 248. | 158 | 316.4 | 196 | 384.8 |
| 7 8 | 44.6 | 45 | 113. | 83 | 181.4 | 121 | 249.8 | 159 | 318.2 | 197 | 386.6 |
| | 46.4 | 46 | 114.8 | 84 | 183.2 | 122 | 251.6 | 160 | 320. | 198 | 388.4 |
| 9 | 48.2 | 47 | 116.6 | 85 | 185. | 123 | 253.4 | 161 | 321.8 | 199 | 390.2 |
| 10 | 50. | 48 | 118.4 | 86 | 186.8 | 124 | 255.2 | 162 | 323.6 | 200 | 392. |
| 11 | 51.8 | 49 | 120.2 | 88 | 190.4 | 125 | 257. 258.8 | 164 | 325.4 | 210 | 410. 428. |
| 12 | 53.6 | 50 | 123.8 | 89 | 190.4 | 127 | 260.6 | 165 | 327.2 $329.$ | 230 | 446. |
| 13 14 | 55·4 57·2 | 52 | 125.6 | 90 | 194. | 128 | 262.4 | 166 | 330.8 | 240 | 464. |
| 15 | 59. | 53 | 127.5 | 91 | 195.8 | 129 | 264.2 | 167 | 332.6 | 250 | 482. |
| 16 | 60.8 | 54 | 129.2 | 92 | 197.6 | 130 | 266. | 168 | 334.4 | 260 | 500. |
| 17 | 62.6 | 55 | 131. | 93 | 199.4 | 131 | 267.8 | 169 | 336.2 | 270 | 518. |
| 18 | 64.4 | 56 | 132.8 | 94 | 201.2 | 132 | 269.6 | 170 | 338. | 280 | 536. |
| 19 | 66.2 | 57 | 134.6 | 95 | 203. | 133 | 271.4 | 171 | 339.8 | 290 | 554. |
| 20 | 68. | 58 | 136.4 | 96 | 204.8 | 134 | 273.2 | 172 | 341.6 | 300 | 572. |
| 21 | 69.8 | 59 | 138.2 | 97 | 206.6 | 135 | 275. | 173 | 343 • 4 | 350 | 662. |
| 22 | 71.6 | 60 | 140. | 98 | 208.4 | 136 | 276.8 278.6 | 174 | 345.2 | 400 | 752. |
| 23 | 73.4 | 61 | 141.8 | 99 | 210.2 | 137 | 280.4 | 175 | 347· 348.8 | 450 | 842. |
| 24 | 75.2 | 63 | 143.0 | 101 | 213.8 | 139 | 282.2 | 177 | 350.6 | 500 | 932. |
| 25 26 | 77· 78.8 | 64 | 147.2 | 102 | 215.6 | 140 | 284. | 178 | 352.4 | | 1112. |
| 27 | 80.6 | 65 | 149. | 103 | 217.4 | 141 | 285.8 | 179 | 354.2 | | 1202. |
| 28 | 82.4 | 66 | 150.8 | 104 | 210.2 | 142 | 287.6 | 180 | 356. | | 1202. |
| 29 | 84.2 | 67 | 152.6 | 105 | 221. | 143 | 289.4 | 181 | 357.8 | | 1382. |
| 30 | 86. | 68 | 154.4 | 106 | 222.8 | 144 | 291.2 | 182 | 359.6 | | 1472. |
| 31 | 87.8 | 69 | 156.2 | 107 | 224.6 | 145 | 293. | 183 | 361.4 | | 1562. |
| 32 | 89.6 | 70 | 158. | 108 | 226.4 | 146 | 294.8 | 184 | 363.2 | | 1652. |
| 33 | 91.4 | 71 | 159.8 | 109 | 228.2 | 147 | 296.6 | 185 | 365. | 950 | 1742. |
| 34 | 93.2 | 72 | 161.6 | 110 | 230. | 148 | 298.4 | 186 | 366.8 | | 1832. |
| 35 | 95. | 73 | 163.4 | III | 231.8 | 149 | 300.2 | 187 | 368.6 | | 1992. |
| 36 | 96.8 | 74 | 165.2 | 112 | 233.6 | 150 | 302. | 188 | 370.4 | 1500 | 2732. |
| 37 | 98.6 | 75 | 167. | 113 | 235.4 | . 151 | 303.8 | 109 | 372.2 | 2000 | 3632. |
| | | | | | | | | | | | |



F16. 50.

Diagram showing the number of pounds per gallon and the number of gallons per ton (2000 lbs.) for liquids of known specific gravity.

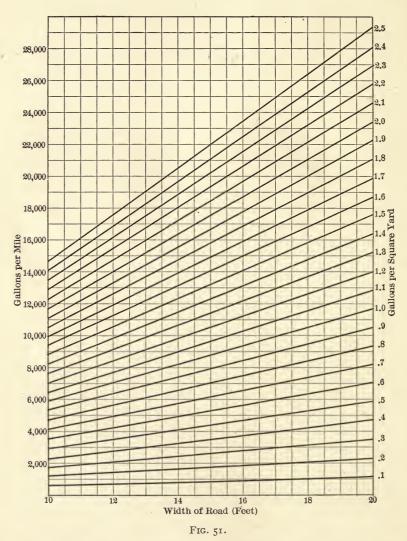


Diagram showing the number of gallons of material required to treat one mile of roadway of known width, at given rates of application per square yard.

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